

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

	PAGE
I.—The Constituents of <i>Rumex Ecklonianus</i> . By FRANK TUTIN and HUBERT WILLIAM BENTLEY CLEWERT	1
II.—Cyanocarone. By REGINALD WILLIAM LANE CLARKE and ARTHUR LAPWORTH	11
III.—The Influence of Water on the Availability of Hydrogen Chloride in Alcoholic Solution. By ARTHUR LAPWORTH and JAMES RIDDICK PARTINGTON	19
IV.—Organic Derivatives of Antimony. Part I. Tricamphorylstibine Chloride and Triphenylstibine Hydroxynitrate and Hydroxysulphate. By GILBERT T. MORGAN, FRANCES M. G. MICKLETHWAIT, and GEORGE STAFFORD WHITEY, B.Sc., A.R.C.S.	34
V.—Experiments on Substituted Allenecarboxylic Acids. Part I. By ARTHUR LAIWORTH and ELKAN WECHSLER	38
VI.—The Production of para-Diazoimides from Alkyl- and Arylsulphonyl-para-diamines. A General Reaction. By GILBERT T. MORGAN and JOSEPH A. PICKARD, B.Sc., A.R.C.S.	48
VII.—The Action of Hydrogen Dioxide on Thiocarbamides. By EDWARD DE BARRY BARNETT	63
VIII.—The Influence of Non-electrolytes on the Solubility of Carbon Dioxide in Water. By FRANCIS LAWRY USHER	66
IX.—The Condensation of Benzaldehyde with Resorcinol. By FRANK GEORGE POPE and HUBERT HOWARD	78
X.—The Relation between the Strengths of Acids and Bases, and the Quantitative Distribution of Affinity in the Molecule. Part II. By BERNHARD FLÜRSCHHEIM	84

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS:

PART I.

Organic Chemistry.

	PAGE
LOSANITSCH (SIMA M.). Electro-syntheses. IV.	i, 1
ENGLER (CARL). Formation of Naphthenes in Mineral Oil	i, 2
ENGLER (CARL) and O. RUTALA. Formation of Naphthenes. II. Action of Aluminium Chloride on Amylene at Low and Moderately High Temperatures	i, 2
ENGLER (CARL) and O. RUTALA. Naphthene Formation. III. Products Formed by Heating Amylene and Hexylene Under Pressure	i, 2
HOFMANN (KARL A.) and HEINZ KIRMSEUTHER. Chloroethylenes	i, 3
HOFMANN (KARL A.), [GRAF] ARMIN ZEDTWITZ, and H. WAGNER. Esters of Perchloric Acid	i, 3
FRANCHIMONT (ANTOINE P. N.). Sodium Alkyl Carbonates	i, 4
PARNASS (JAKOB). Kephalin	i, 4
RAMBERG (LUDWIG). α -Bromopropionic Acid	i, 4
CARLINFANTI (EMILIO) and MARIO LEVI-MALVANO. Melting and Solidifying Points of Fatty Substances. I. Binary Mixtures of Stearic, Palmitic, and Oleic Acids	i, 5
CARLINFANTI (EMILIO) and MARIO LEVI-MALVANO. Melting and Solidifying Points of Fatty Substances. II. Ternary Mixtures of Palmitic, Stearic, and Oleic Acids	i, 6
WEGSCHEIDER (RUDOLF). Hydrolysis of Fats and Oils	i, 6
SPRING (WALTHER). Detergent Action of Soap Solutions. Part II.	i, 6
GEORGES IMBERT and CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE. Hydroxyaliphatic Acids from the Products of the Interaction of Hypochlorous Acid or Chlorine and the Glycerides of Aliphatic Acids of Animal or Vegetable Origin	i, 7
FEIST (FRANZ). Stereochemistry of the Glutaconic Acid Group	i, 7
FEIST (FRANZ) and G. POMME. Stereoisomeric α -Methylglutaconic Acids	i, 9
FEIST (FRANZ) and R. REUTER. α -Dimethylglutaconic Acids	i, 9
LOQUIN (RENÉ). Derivatives of Propylsuccinic Acid	i, 10
SCHENCK (MARTIN). Cholic Acid. I.	i, 10
LEVY (PAUL). American Colophony	i, 11
SENDRENS (JEAN B.). Catalytic Preparation of Unsymmetrical Aliphatic Ketones	i, 11
SALKIND (JULIUS) and (Madame) T. BEBERSCHWILL. Synthesis of Ketones by means of Organo-magnesium Compounds	i, 11
YOUNG (WILLIAM J.). The Hexosephosphate Formed by Yeast-Juice from Hexose and a Phosphate	i, 12
GUTHRIE (ALEXANDER) and FR. BAURIEDEL. Platinum	i, 12
JONES (LAUDER WILLIAM) and RALPH OESPER. Preparation of Hydroxamic Acids from Hydroxylamine Salts of Organic Acids	i, 13
ROSENHEIM (ARTHUR). Reaction between Hydrogen Sulphide and Cyanaminodithiocarbonates	i, 13
BRAUN (JULIUS VON). Dithiourethanes. II. Preparation of Thioglycols from Bisdithiourethanes	i, 13
SÖLL (JULIUS) and ALBERT STUTZER. Compounds from Guanylearbamide and Diguamide	i, 14
ULTÉE (A. J.). Action of Hydrogen Chloride on Acetone Cyanohydrin	i, 14
RUPF (HANS) and SIDONIUS KESSLER. Constitution and Behaviour of Semicarbazidesemicarbazones	i, 15

	PAGE
HOFMANN (KARL A.) and HEINZ KIRMREUTHER. Metallic Derivatives of Chloro- and Bromo-acetylene	i, 16
WHEELER (HENRY L.) and LEONARD M. LIDDLE. Halogen-amino-acids. VI. Iodo-derivatives of <i>p</i> -Toluidine. 3:5-Di-iodo-4-aminobenzoic Acid	i, 17
WHEELER (HENRY L.) and LEONARD M. LIDDLE. Halogen-amino-acids. VII. Iodine Derivatives of <i>o</i> -Toluidine. 3-Iodoaminobenzoic Acids	i, 19
ROMBURGH (PIETER VAN). Nitration of Diethylaniline	i, 19
WERNER (ALFRED). Colour and Constitution	i, 20
FIGHTER (FRITZ) and WALTER BERNOULLI. Electrolytic Reduction of 2-Nitrotoluene-4-sulphonyl Chloride	i, 20
TINGLE (J. BISHOP) and C. E. BURKE. Nitration. VI. Nitroaniline Derivatives of Organic Acids	i, 21
FISCHER (HANS). <i>d</i> -Leucyl-L-tryptophan	i, 22
PIUTTI (ARNALDO). Maleic and Fumaric Derivatives of <i>p</i> -Aminophenols	i, 22
KÖTZ (ARTHUR) and TH. GRETHE. $\Delta^{1:2}$ -Dihydrophenol or Δ^2 -cyclo-Hexenone	i, 24
BRAUN (JULIUS VON) [and A. TRÜMLER]. Synthesis of Octa-, Deca-, and Dodeca-methylene Compounds of the Aliphatic Series	i, 25
WOHLBBEEN (WILLIAM J.). Monohalogenphenols	i, 27
WOLFFENSTEIN (RICHARD) and OSKAR BOETERS. Preparation of Aromatic Nitrohydroxy-compounds	i, 27
CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING). Preparation of Arylalkyl- <i>p</i> -aminophenols	i, 28
OBERMILLER (JULIUS). Estimation of Ortho- and Para-Sulpho-groups in Phenolsulphonic Acids	i, 28
VRIES (OTTO DR.). Abnormal Reduction of an Aromatic Nitro-compound with Tin and Hydrochloric Acid and an Interesting Case of Dimorphism	i, 29
FIGHTER (FRITZ) and OTTO WALTER. 2:5-Diphenylphenol	i, 29
SCHMIDT (JULIUS) and HERMANN STÜTZEL. The Fluorene Series. I.	i, 29
TSCHUGAREFF (LEO) and A. GASTEFF. Cholesterol. I. The Xanthogen Reaction	i, 31
CHEMISCHE WERKE VORM. DR. HEINRICH BYK. Preparation of Cholesteryl α -Bromo α -valerate	i, 31
KLOBB (TIMOTHÉE). Phytosterols in the Family of <i>Synantherea</i> . Faradiol, a New Dihydric Alcohol from Coltsfoot	i, 31
TARBOURIECH (P. JOSEPH). Dehydration of cycloHexanolpropan- β -ol	i, 32
BREDT (JULIUS) and K. MAY. New Method of Preparation of Tricyclene-carboxylic Acid (Dehydrocamphenylic Acid)	i, 32
FRITZSCHE (FRANZ) & Co. Preparation of <i>n</i> -Propyl <i>p</i> -Aminobenzoates	i, 32
MANCHOT (WILHELM) and J. R. FURLONG. Isomerism by Anils (Schiff's Bases)	i, 33
HOUBEN (JOSEF), ARNOLD SCHOTTMÜLLER, and ROBERT FREUND. Synthesis of Aromatic Amino-acids by Rearrangements. III. Alkyl-aminotoluic Acids	i, 34
BOESCHE (WALTHER). Addition of Ethyl Phenylacetate to Unsaturated Compounds	i, 35
LIEBERMANN (CARL) and H. TRUCKSÄSS. <i>allo</i> - and <i>iso</i> -Cinnamic Acids	i, 36
HELLER (GUSTAV) and WALTER TISCHNER. Bromination of <i>o</i> -Nitrophenyl-propionic Acid	i, 37
CHEMISCHE FABRIK VON HEYDEN. Preparation of <i>o</i> - α -Trichloroacetoxybenzoic Acid	i, 37
CHEMISCHE FABRIK VON HEYDEN. Preparation of Aromatic Halogen-alkyloxycarboxylic Acids	i, 37
SPALLINO (ROSARIO) and G. PROVENZAL. Preparation of <i>o</i> -Thymotic Acid and of Certain of its Derivatives	i, 38
FRANCESCONI (LUIGI) and GUIDO CUSMANO. Action of Free Hydroxylamine on Coumarin	i, 38
BUCHER (JOHN E.) and W. CLIFTON SLADE. Anhydrides of <i>iso</i> Phthalic and Terephthalic Acids	i, 38
FEIST (FRANZ) and G. POMME. β -Phenylglutaconic Acid	i, 39

	PAGE
BARGEGLINI (GUIDO) and S. SILVESTRI. Action of Sulphuric Acid on Santonin. II.	i, 39
BAZLEN (MAX). Benzaldehydesulphoxylates	i, 40
KALLE & Co. Preparation of <i>p</i> -Methoxysalicylaldehyde from <i>p</i> -Hydroxy-Salicylaldehyde	i, 40
GUYOT (ALFRED) and A. GUY. New Syntheses of Vanillin	i, 40
PATERNÒ (EMANUELE) and G. CHIEFFI. Organic Syntheses by means of Sunlight. IV. Action of Paraffins and Homologues of Benzene on Ketones and Aldehydes	i, 41
MONTAGNE (P. J.). 2:4:6-Tribromobenzophenone	i, 42
VOSWINCKEL (HUGO). Derivatives of Catechol	i, 42
STOBBE (HANS). Relationship between the Colour and Constitution of Unsaturated Ketones and their Salts	i, 43
STOBBE (HANS) and RICHARD HÄRTEL. Light Absorption, Basicity, Constitution, and Salts of Ketones of the Dibenzylidenacetone [Distyryl Ketone] and Dibenzylidenecyclopentanone Series	i, 43
STOBBE (HANS) and SIEGFRIED SEYDEL. Light Absorption, Basicity, Constitution, and Salts of Certain Unsaturated Cyclic Ketones, Ketone Acids, and Ketone Esters	i, 45
STAUDINGER (HERMANN) [and, in part, with J. BUCHWITZ]. Ketens. XIII. Action of Diphenylketen on Carbonyl Derivatives	i, 46
TORREY (HENRY A.) and C. M. BREWSTER. Phenylhydrazones of 2-Acetyl-1-naphthol [1-Hydroxy- <i>β</i> -naphthyl Methyl Ketone]: Alkali-insoluble Naphthols	i, 47
LESER (GEORGES). Two Isomeric <i>cyclo</i> Hexane <i>β</i> -Diketones	i, 48
HAACK (HERMANN). Quinhydrone from Chloranil and Aromatic Hydrocarbons	i, 48
BADISCHE ANILIN- & SODA-FABRIK. Preparation of Halogenated Anthraquinones	i, 49
FABENFABRIKEN VORM. FRIEDRICH BAYER & Co. Preparation of Halogenated Nitroanthraquinones	i, 49
FABENFABRIKEN VORM. FRIEDRICH BAYER & Co. [Preparation of Thioglycine Derivatives of Anthraquinone]	i, 49
VOSWINCKEL (HUGO) and FRITZ DE WEERTH. The Naphthacene Series. III.	i, 49
CUSMANO (GUIDO). Stereo- and Structural Isomerides obtained by the Introduction of Acyl Radicles into <i>β</i> -Hydroxylamines. I.	i, 50
KOMPPA (GUSTAV). Syntheses in the Camphor and Terpene Series. II. Complete Synthesis of Camphoric Acid and Camphor	i, 51
GUERBET (MARCEL). Condensation Products from Camphor	i, 52
DARMOIS (EUGENE). Composition of Oil of Turpentine	i, 52
VAYON (G.). Hydrogenation in the Terpene Series	i, 52
ACWERS (KARI). [<i>α</i> -Terpinene]	i, 53
SEMMLER (FRIEDRICH W.) and ENDRE SCHÖSSBERGER. Constituents of Ethereal Oils. I. Terpinolene. II. Terpinene	i, 53
KIMURA (H.). <i>Cryptomeria Japonica</i> Oil	i, 53
PERRIER (GUSTAVE) and A. FOUCHER. Volatile Oil of <i>Rhus Cotinus</i> ("Young Fustic")	i, 54
COLWELL (HECTOR A.). Catalytic Oxidation of Guaiacum Resin by Copper	i, 54
MEULEN (HENRI FER). Preparation of Indican	i, 54
LAIDLAW (PATRICK P.). Active Principle of a Benin Spear Poison	i, 54
LIPPMAHN (EDMUND O. von). Discovery of the Optical Activity of Tannin	i, 55
JOLKVER (Mlle. EUGENIE). Furfurylpropylcarbinol	i, 55
MARSHAUK (CHARLES). 4-Benzylcumarin	i, 55
GOMBURG (MOSES) and LEE H. CÖNE [with O. B. WINTER]. Triphenylmethyl. XVIII. Quinocarbinium Salts	i, 55
FERRARIO (ENCS) and M. NEUMANN. 3:6-Dimethylfluoran	i, 59
BADISCHE ANILIN- & SODA-FABRIK. Preparation of 2:3-Diketodihydro-(1)-thionaphthen Derivatives	i, 69

CONTENTS.

v

	PAGE
BADISCHE ANILIN- & SODA-FABRIK. Preparation of Derivatives of 2:3-Diketodihydro-(1)-thionaphthens	i, 60
AUTENRIETH (WILHELM) and FRITZ BEUTTEL. Poly-membered Heterocyclic Systems containing Sulphur, and Ring Closure in the Para-Position	i, 60
AUTENRIETH (WILHELM) and FRITZ BEUTTEL. Poly-membered Heterocyclic Systems containing Sulphur, and Ring Closure in the Meta-Position	i, 61
GORDIN (HARRY M.). Crystalline Alkaloid of <i>Calycanthus Glauco</i> . III. <i>iso</i> Calycanthine, Isomeric with Calycanthine	i, 62
GAUBERT (PAUL). A New Highly Fluorescent Substance Derived from Physostigmine [Eserine]	i, 62
SCHULZE (ERNST) and G. TRIER. Constitution of Stachydrine	i, 62
PLANCHER (GIUSEPPE) and D. GIUMELLI. Synthesis of Indolenine Ketones	i, 63
DANZENS (GEORGES). Catalytic Hydrogenation of Aromatic and Quinoline Bases	i, 63
EDINGER (ALBERT) and L. BÜHLER. <i>B</i> -Sulphoquinolinecarboxylic Acids	i, 64
HELLER (GUSTAV) and WALTER TISCHNER. Reduction of <i>o</i> -Nitrophenyl-propionic Acid	i, 64
BORSCHKE (WALTHER) and J. CAMPER TIRISNGH. Condensation of α -Diketones with Aldehydes and Primary Arylamines	i, 65
PICCARD (JEAN). Auxochromic Action of Amino- and Aminophenyl Groups	i, 66
PICCARD (JEAN). A Reaction of Polybasic Acids and a New Reaction for Titanium	i, 67
ROSENKUND (KARL W.). Diketodialkylpiperazines	i, 67
JOHNSON (TREAT B.). Pyrimidines. XLVIII. Synthesis of 5-Cyano-uracil	i, 69
AUWERS (KARL) and H. VOSS. Influence of Constitution on the Conversion of Phenylhydrazones of Unsaturated Compounds into Pyrazolines	i, 70
RUPE (HANS) and K. G. THIES [and, in part, with ALEX. WETTER]. Benzoylenetbenzimidazole	i, 71
GRANDMOUGIN (EUGÈNE) and ED. DESSOULAVY. Indigotin. II. Indigotin-diarylimides	i, 73
GRANDMOUGIN (EUGÈNE). Indigotin. III. 5:7:5':7'-Tetrabromo-indigotin	i, 74
ULLMANN (FRITZ) and ROBERT HEISLER. Preparation of Azines from Nitroso- β -naphthols and <i>o</i> -Phenylenediamine	i, 74
BUSCH (MAX). Function of the Nitrogen Atoms in Primary Hydrazines	i, 75
BUSCH (MAX) and JOHANNES REINHARDT. Addition of Thiocarbimides to Ring-substituted Arylhydrazines	i, 75
PUMMERER (RUDOLF) and MAX GOETTLER. Isatinamils. I. Isatin-dimethylamino-2-anil. Its Formation, Hydrate, and Salts	i, 77
FARBERKE VORM. MEISTER, LUCIUS & BRÜNING. Preparation of 1- <i>p</i> -Dialkylaminophenyl-2:4-dimethyl-3-hydroxymethyl-5-pyrazolones.	i, 78
FARBENFABRIKEN VORM. FRIEDRICH BAYER & CO. Preparation of Xanthine and Guanine Derivatives containing Substituents in Position 8	i, 78
RASSOW (BERTHOLD) and OTTO BAUMANN. Hydrazo-compounds. IV. Reactions of Hydrazobenzene with Aliphatic Aldehydes and with Benzoyl Chloride	i, 79
BÜLOW (CARL) and KARL HAAS. Synthetical Experiments on the Preparation of Derivatives of Hetero-condensed-heterocyclic "1:3-Triazo-7:0'-pyrimidine" [1:3:7:9-Benzotetrazole]	i, 80
BÜLOW (CARL). Hetero-condensed, Heterocyclic Compounds with Two Nuclei: Substituted "Tetrazotopyrimidines"	i, 81
CHEMISCHE WERKE VORM. DR. HEINRICH BYK. Preparation of a Soluble Double Compound of Theophylline and Piperazine	i, 81

	PAGE
MORUZZI (GIOVANNI). The Gelatinisation of Egg-Albumin by Hydrochloric Acid. I.	i, 81
CHAPMAN (H. G.) and J. M. PETRIE. The Hexone Bases from White of Egg	i, 82
DIETRICH (M.). The Caseinogen-Peptones containing Phosphorus	i, 82
TAYLOR (ALONZO E.). Synthesis through Ferment Action	i, 82
TAKEMURA (M.). Action of Proteolytic Enzymes on Protamines	i, 82
KOHL (FRIEDRICH G.). Reversibility of Enzyme Actions and the Effect of External Factors on Enzymes (Invertase, Maltase)	i, 82
HUDSON (C. S.) and H. S. PAINE. Hydrolysis of Salicin by the Enzyme Emulsin	i, 83
SCHMIDT-NIELSEN (SIGNE) and SIGVAL SCHMIDT-NIELSEN. Influence of Acids on the Loss of Activity of Rennet Caused by Shaking	i, 83
EULER (HANS) and IVAR BOLIN. Chemical Composition and Biological Function of an Oxydase	i, 84
FAERWERKE VORM. MEISTER, LUCIUS & BRÜNING. Preparation of Derivatives of Phenylarsenious Oxide and of Arsenobenzene	i, 84

PART II.

General and Physical Chemistry.

BECKMANN (ERNST) and PERCY WAENTIG. Photometric Measurements with the Coloured Bunsen Flame	ii, 1
DECHEND (HERMANN VON). Spectral Analytical Investigation of the Glow Light at Points	ii, 2
BOISBAUDEAN (P. E. LECOQ DE). Band Spectra of Barium and Aluminium	ii, 3
PASCHEN (FRIEDRICH). Systems of Series in the Spectra of Zinc, Cadmium, and Mercury	ii, 3
PURVIS (JOHN F.). Influence of Dilution on the Colour and the Absorption Spectra of Various Permanganates	ii, 3
BYK (ALFRED) and H. JAFFE. Relations between Constitution and Absorption towards the Violet End of the Spectrum for Solutions of certain Chromium and Iron Salts	ii, 3
STOEBE (HANS), RICHARD HARTTEL, and SIEGFRIED SEYDEL. Relationship between the Colour and Constitution of Unsaturated Ketones and their Salts	ii, 4
GAUBERT (PAUL). Polychroism of Artificially Coloured Crystals	ii, 4
POCHETTINO (ALFREDO). Luminescence Phenomena in Certain Organic Compounds	ii, 5
WILKINSON (JOHN ANDERSON). Phosphorescence of some Inorganic Salts	ii, 5
WHIDDINGTON (R.). Electrical Behaviour of Fluorescing Iodine Vapour	ii, 6
EVEREST (A. E.). Optical Activity of the Asymmetric Atom	ii, 6
PADOA (MAURICE). Attempts at Asymmetric Synthesis by means of Circularly-polarised Light	ii, 6
WARBURG (EMIL). Photochemical Action. II.	ii, 6
SZILARD (BÉLA). Apparatus for Measuring Radioactivity	ii, 7
MADSEN (JOHN P. V.). The Scattering of the β -Rays of Radium	ii, 7
SCHMIDT (HEINRICH W.). Passage of β -Rays through Matter	ii, 7
HAHN (OTTO) and LISE MEITNER. Law of Absorption of the β -Rays	ii, 8
BARCLAY (CHARLES G.). Phenomena of X-Ray Transmission	ii, 8
SACKEDOTE (PAUL). Alteration in the Colour of the Diamond under the Action of Various Physical Agents	ii, 8
MEYER (ANDRÉ). Influence of Radium X-Rays and Cathode Rays on Various Precious Stones	ii, 9

	PAGE
BRAUNS (R.). Influence of Radium Rays on the Coloration of Sanidin, Zircon, and Quartz. Crystalline Form of the Zircon in Sanidinite from the Leacher See . . .	ii, 9
STRUTT (ROBERT J.). Accumulation of Helium in Geological Time. II. . .	ii, 9
SODDY (FREDERICK). The Relation between Uranium and Radium. IV. . .	ii, 10
SODDY (FREDERICK). The Rays and Products of Uranium-X . . .	ii, 10
LUSBY (S. G.). Experimental Study of the Large Ions in the Air . . .	ii, 10
POLLOCK (JAMES A.). Mobility of the Large Ions in the Air . . .	ii, 11
METCALFE (E. PARR). Ionisation in Various Gases . . .	ii, 11
BROGLIE (MAURICE DE) and L. BRIZARD. Chemical Reactions and the Ionisation of Gases . . .	ii, 11
SCHAEFFER (OSCAR C.) and HERMAN SCHLUNDT. Dielectric Constants of the Halogen Hydrides . . .	ii, 12
PRIDEAUX (EDMUND B. R.). Relation between Composition and Conductivity in Solutions of Meta- and Ortho-phosphoric Acids . . .	ii, 12
WHITE (GEORGE F.) and HARRY C. JONES. Effect of Temperature and Dilution on the Conductivity of Organic Acids in Aqueous Solution . . .	ii, 13
RIESENFELD (ERNST H.) and B. REINHOLD. Transport Number of Hydrochloric Acid . . .	ii, 14
RIESENFELD (ERNST H.) and B. REINHOLD. Determination of Transport Numbers from <i>E.M.F.</i> Measurements in Solvents which are only Partially Miscible with Water . . .	ii, 14
DENISON (ROBERT B.). Relative Rates of Migration of Ions in Aqueous Solution. I. . .	ii, 15
WEISS (J.) and J. KOENIGSEBERGER. Thermo-electric Forces of Certain Metallic Oxides and Sulphides . . .	ii, 15
MERCZYNG (H.). Very Short Electromagnetic Waves. Anomalous Reflexion and Dispersion of Liquids . . .	ii, 15
MEUNIER (JEAN). Conditions Necessary for Maintaining Platinum in a State of Incandescence in the Interior of a Bunsen Burner . . .	ii, 15
RENGADE (ÉTIENNE). Theoretical Cooling Curves of Binary Mixtures . . .	ii, 16
RENGADE (ÉTIENNE). Theoretical Form of the Cooling Curves of Binary Mixtures. The Case of Solid Solutions . . .	ii, 17
TAMMANN (GUSTAV). Superheating of Crystals . . .	ii, 17
STOLTZENBERG (H.). Melting-point Apparatus which can also be Used for the Determination of Solubilities with small Quantities of Substance . . .	ii, 17
OLIVARI (F.). Iodine as a Cryoscopic Solvent . . .	ii, 18
ROLLA (LUIGI). Vapour Pressures at Low Temperature . . .	ii, 19
TIMMERMANS (J.). Critical Phenomena of Solution . . .	ii, 19
RICHARDS (THEODORE W.). Recent Investigations in Thermochemistry . . .	ii, 19
COWPER (ALFRED DENNY) and GUSTAV TAMMANN. Alteration of Compressibility with the Softening of an Amorphous Substance . . .	ii, 20
TRAUBE (ISIDOR). Connexion of Surface-tension with the Internal Pressure and van der Waals' Constants α and β . . .	ii, 20
HOSKING (RICHARD). Viscosity of Water . . .	ii, 20
GUYE (CHARLES E.) and V. FREDERICKSZ. Viscosity of Solids at Low Temperatures . . .	ii, 21
MCBAIN (JAMES W.). Mechanism of the Adsorption ("Sorption") of Hydrogen by Carbon . . .	ii, 21
KLEEMAN (K. D.). Relations between the Critical Constants and Certain Quantities connected with Capillarity . . .	ii, 22
GARTER (M. M.). Kinetic Interpretation of Osmotic Pressure . . .	ii, 22
BILTZ (WILHELM) and ARVED VON VEGERACK. Osmotic Pressure of Colloids. I. Function of Electrolytes in the Dialysis of Colloids . . .	ii, 22
WENK (W.). Influence of Substances in Solution on the Velocity of Crystallisation and the Crystal-habit of Potassium Sulphate . . .	ii, 23
FOCK (ANDREAS). Isomerism and Polymorphism . . .	ii, 23
SVEDBERG (THE). Preparation of Colloidal Solutions by the Disintegration of Metals by Ultra-violet Light . . .	ii, 23

	PAGE
MULLER (JOSEPH A.). Phase Rule	ii, 24
SMITS (ANDREAS). Photo- and Electro-chemical Equilibria	ii, 24
TRAUTZ (MAX). Temperature-coefficient of Chemical Reaction Velocities. IV. The Velocity Isochore of Gas- Reactions, its Connexion with that of the Reactions of Free Atoms, with Applications	ii, 24
VELEY (VICTOR H.) [in part, with JOHN C. CAIS]. Rate of Evolution of Gases from Homogeneous Liquids	ii, 25
EULER (HANS) and BETH AF UGGLAS. Hydrolysis and Reaction Velocity in Mixtures of Alcohol and Water	ii, 25
BEVERIDGE (MISS HEATHER HENDERSON). Hydrolysis of Salts of Amphoteric Electrolytes	ii, 25
LORING (F. H.). Atomic Weights as Mathematical Functions	ii, 26
HINRICHS (GUSTAV D.). Calculation of Atomic Weights. Solution of the Equation of Condition	ii, 26
NOTES (WILLIAM A.). Molecular Rearrangements	ii, 27

Inorganic Chemistry.

RICHARZ (FRANZ). Anodic Formation of Hydrogen Peroxide	ii, 27
FALKENSTEIN (KURT VOGEL VON). Dissociation of Hydrogen Bromide and Hydrogen Iodide at High Temperatures	ii, 27
HILL (ERNEST G.) and ANNODA P. SIKKAR. Electric Conductivity and Density of Solutions of Hydrogen Fluoride	ii, 27
AUBEL (EDMOND VAN). Production of Ozone by Ultra-violet Light	ii, 28
CALLENDAR (HUGH L.) and HERBERT MOSS. Boiling Point of Sulphur Corrected by Reference to New Observations on the Absolute Expansion of Mercury	ii, 28
KRUYT (HUGO R.). The Dynamic Allotropy of Selenium	ii, 28
FOX (CHARLES J. J.). Coefficients of Absorption of Nitrogen and Oxygen in Distilled Water and Sea-Water, and of Atmospheric Carbon Dioxide in Sea-Water	ii, 29
STOCK (ALFRED) and FRANZ GOMOLKA. Red Phosphorus and the so-called "Hitton's Phosphorus."	ii, 30
JORISSEN (WILLEM P.) and N. H. SIKWERTZ VAN REESEMA. Oxidation of Phosphorus	ii, 31
CAVALIERE (JACQUES) and E. CORNEC. Preparation of Hypophosphoric Acid	ii, 31
BACH (ALEXIS). Decomposition of Water by Hypophosphites in Presence of Palladium as a Catalyst	ii, 31
BLOCH (LÉON). Phosphorescent Oxidation of Arsenic	ii, 32
FIELDING (W.). Formation of Silicon Sulphide in the Desulphurisation of Iron	ii, 32
KARANDJEFF (B.). Thermal Analysis of the System K_2SO_4 -KF	ii, 33
RIESENFELD (E. H.) and B. REINHOLD. Existence of Real Percarbonates and their Differentiation from Carbonates with Hydrogen Peroxide of Crystallisation	ii, 33
COLSON (ALBERT). Reduction of Sodium Sulphate by Carbon	ii, 34
DAUTRICHE (H.). Action of Safety Explosives containing Ammonium Nitrate in the Presence of Carbon, Paper, and Paraffin	ii, 34
DUBREUIL (LOUIS). True Atomic Weights. Stas' Determinations. III.	ii, 34
BOSE (MARGARETE). So-called Electrolytic Peroxide of Silver	ii, 34
DELÉPINE (MARCEL). Silver and Thallium Iridichlorides and Irido- chlorides	ii, 34
KOLB (ADALBERT). The Calcium Silicides and their Absorptive Power for Nitrogen	ii, 35
HILPERT (SIE-FRIED) and ERNST KOHLMEYER. Calcium Ferrites	ii, 35
MOESER (LUDWIG) and H. BORCK. Compounds containing Iron Peroxide, FeO_2	ii, 36

	PAGE
LEVY-MALVANO (MARIO). Hexahydrated Glucinum Sulphate	ii, 37
ROBINSON (WILLIAM O.) and W. H. WAGGAMAN. Basic Magnesium Chlorides	ii, 37
COHEN (ERNST) and KATSUJI INOUE. Zinc Amalgams	ii, 37
EPHRAIM (FRITZ) and LEONID HEYMANN. Double Fluorides of Univalent Thallium	ii, 37
FIELD (SAMUEL). Conditions which Determine the Composition of Electro-deposited Alloys. Part I. Copper-Zinc Alloys	ii, 38
FRIEND (J. NEWTON). The Corrosion of Iron	ii, 39
FRIEND (J. NEWTON). The Action of Air and Steam on Pure Iron	ii, 39
HILBERT (STIEGFRIED). Reduction of Iron Oxide by Hydrogen and Carbon Monoxide	ii, 39
RIESENFELD (E. H.) and F. SEEMANN. Chromi-aquo-triammines	ii, 39
MECKLENBURGH (WERNER). The Isomerism of the Stannic Acids	ii, 41
EPHRAIM (FRITZ) and S. WEINBERG. Double Halogenides of Ter-, Quadri-, and Quinque-valent Antimony	ii, 41
MCCAUGHEY (W. J.). Effect of Ferric and Cupric Salt Solutions on Gold	ii, 42
THOMAS (CARL). Gold Hydrosols	ii, 42
URAZOFF (G. G.). Magnesium Aurides	ii, 43
ARCHIBALD (EBENEZER H.). Atomic Weight of Platinum	ii, 43
DELEPINE (MARCEL). Metallic Iridium Disulphates	ii, 44
GUTHRIE (ALEXANDER) and K. MAISCH. Osmium	ii, 45

Mineralogical Chemistry.

RAKUSIN (MICHAEL). The Need for a Systematic Study of Optically Active Petroleum	ii, 45
PILIPENKO (P. P.). Selenium in Altai Minerals	ii, 45
LADY (T. H.). A Pitchblende probably occurring in New South Wales	ii, 46
LACROIX (ALFRED). Rhodizite in the Pegmatites of Madagascar	ii, 46
GRIFFITHS (E.). Fuchserite from West Australia	ii, 47
PALACHE (CHARLES) and H. E. MERWIN. Connellite and Chalcophyllite from Bisbee, Arizona	ii, 47
HAUSER (OTTO) and FRITZ WIRTH. The Earths of Euxenite	ii, 47
PILIPENKO (P. P.). Bertrandite from Altai	ii, 48
SERRA (AURELIO). Sardinian Minerals: Species from the Province of Sassari	ii, 48
BROUWER (H. A.). Lujaurites from Pilandsberg (Transvaal)	ii, 48
LACROIX (ALFRED). Rhönite from Puy de Barneire at Saint-Sandoux	ii, 49
LEITMEIER (HANS). Deposits from the Mineral Water of the Rohitsch Springs, Styria	ii, 49

Physiological Chemistry.

KAYA (R.) and ERNEST H. STARLING. Asphyxia in the Spinal Animal	ii, 50
BUCKMASTER (GEORGE A.) and JOHN A. GARDNER. Supposed Presence of Carbon Monoxide in Normal Blood and in the Blood of Animals Anesthetised with Chloroform	ii, 50
PALADINE (RAFFAELE). Comparison of the Hæmoglobin of certain Molluscs with that of Vertebrates	ii, 50
BARCROFT (JOSEPH) and W. O. R. KING. Effect of Temperature on the Dissociation Curve of Blood	ii, 50
GEOS (OSCAR). Hæmolysis	ii, 51
DEETJEN (H.). The Disintegration and Life of Blood-platelets	ii, 51
LETSCHKE (EUGEN). Spectro-photometry of Blood	ii, 52
BEGLIA (GIUSEPPE) and L. KARCZAG. Influence of Stereochemical Configuration on Certain Physico-chemical Properties of Organic Colloids	ii, 52

	PAGE
ARRHENIUS (SVANTE). The Laws of Digestion and Absorption	ii, 52
SCHITTENHELM (ALFRED). The Enzymes concerned in Nuclein Metabolism in Human Organs	ii, 52
FRANK (FRANZ) and ALFRED SCHITTENHELM. The Fate of Nucleic Acid contained in the Food of Normal Men	ii, 52
SCHITTENHELM (ALFRED) and KARL WIENER. The Occurrence and Importance of Allantoin in Human Urine	ii, 52
SCHITTENHELM (ALFRED). The Enzymes Concerned in Nuclein Metabolism in Lupin Seedlings	ii, 52
LEVENE (PHOEBUS A.) and G. M. MEYER. The Elimination of Total Nitrogen, Urea, and Ammonia following the Administration of Amino-acids, Glycylglycine, and Glycylglycine Anhydride	ii, 53
LEVIN (ISAAC), D. D. MANSON, and PHOEBUS A. LEVENE. The Influence of Removal of Segments of the Gastrointestinal Tract on the Character of Protein Metabolism	ii, 53
IZAR (GUIDO). The Influence of Certain Mercury Compounds on Metabolism	ii, 53
RUEHLAND (W.). [The Permeability of Cells for Dyes]	ii, 53
MCCLENDON (J. E.). Nucleo-protein in the Yolk Platelets of the Frog's Egg; and the Black Pigment	ii, 54
LYON (ELIAS P.). The Catalase of Echinoderm Eggs before and after Fertilisation	ii, 54
KOCH (WALDEMAR). [Analyses of Brains. Distribution of Sulphur in Brains]	ii, 54
KOCH (WALDEMAR) and FRED. W. UPSON. [Analyses of Brains. Distribution of Sulphur in Brains]	ii, 54
LILJESTRAND (G.). The Action of Certain Salts on Frog's Motor Nerves	ii, 54
TEUNBERG (TORSTEN). Influence of Different Substances on the Gaseous Exchange of the Surviving Muscular Tissue of Frogs. I. and II.	ii, 54
HANSEN (OLAV). The Formation of Carbon Dioxide in Surviving Tissues	ii, 55
MEIGS (EDWARD B.). Water Rigor in Frog's Muscle	ii, 55
VELEY (VICTOR H.) and AUGUSTUS D. WALLER. Action of Cinchona Alkaloids on Muscle	ii, 55
KUTSCHER (FRIEDRICH). Extractives of Fish Muscle	ii, 55
SALKOWSKI (ERNST). The Occurrence of Inactive Lactic Acid in a Meat Extract	ii, 55
SATO (T.). The Nucleo-protein of Spleen	ii, 56
BOTTAZZI (FILIPPO) and NOÉ SCALINCI. Chemico-physical Investigations on the Crystalline Lens. XI. Imbibition of the Lens in Water at Different Temperatures and in Acids and Alkalis	ii, 56
QUACCIARIELLO (G.). Chemico-physical Investigations on the Crystalline Lens	ii, 56
GASSMANN (TH.). Chemical Investigation of Teeth. II.	ii, 57
HAAS (PAUL). Inorganic Constituents of Two Egyptian Mummies	ii, 57
SARTHOFF (J.). Presence of an AEROXYDASE and Catalase in Milk	ii, 57
BORDAS (FRÉD.) and TOUPIAIN. AEROXYDASE and Catalase in Milk	ii, 57
LAQUER (WALTHER). Can the Radium Emanations taken up by Drinking be Detected in the Urine?	ii, 58
SATO (T.). The Origin of Ethereal Sulphates in the Organism	ii, 58
ELLIS (G. W.) and JOHN A. GARDNER. The Origin and Destiny of Cholesterol in the Animal Organism. VI. The Excretion of Cholesterol by the Cat	ii, 58
GLEHN (W.). The Biological Significance of Lecithin. IV. The Blood-Content of Phosphorus and Iron in Lipoid Form in Cases of <i>Polycythaemia rubra megalosplenica</i>	ii, 58
EBERFELD (RICHARD) and WILHELM KULKA. The Detection of Phosphorus and Hypophosphorous Acids in Organs after Phosphorus Poisoning. II.	ii, 59
WATERMAN (N.). <i>d</i> -Suprarenine (<i>d</i> -Adrenaline)	ii, 59

	PAGE
FRANKL (THEODOR). The Antagonism between Adrenaline and the Chlorides of the Alkaline Earths and of Potassium . . .	ii, 59
HILL (A. V.). Mode of Action of Nicotine and Curare, determined by the Form of the Contraction Curve and the Method of Temperature-coefficients . . .	ii, 59
WOODRUFF (LORANDE LOSS) and HERBERT HORACE BUNZEL. Relative Toxicity of Various Salts and Acids towards <i>Paramecium</i> . . .	ii, 59

Chemistry of Vegetable Physiology and Agriculture.

BRASCH (WALTHER). The Degradation by Bacteria of the Ultimate Hydrolysis Products of Proteins . . .	ii, 60
KOCH (ALFRED). Accumulation of Nitrogen in Soils by Free Bacteria . . .	ii, 60
MAZÉ (PIERRE). Production of Citric Acid by <i>Citromyces</i> . . .	ii, 60
WEHMER (CARL). Fungi which Produce Citric Acid . . .	ii, 61
REICHEL (HEINRICH). Theory of Disinfection. I. The Disinfecting Action of Phenol. III. . .	ii, 61
BERNADINI (LUIGI) and A. SINISCALCHI. Influence of Varying Relations between Lime and Magnesia on the Growth of Plants . . .	ii, 61
TREBOUX (O.). Formation of Starch from Sorbitol in <i>Rosaceae</i> . . .	ii, 61
YOUNG (VALENTIN). Influence of Aluminium Salts on the Colour of Flowers . . .	ii, 62
OSTERHOUT (W. J. V.). Protective Action of Sodium for Plants . . .	ii, 62
HINRICHSSEN (F. WILLY) and ERICH KINDSCHER. Molecular Complexity of Caoutchouc in the Milk . . .	ii, 62
HECKEL (ÉDOUARD). Influence of Anesthetics and of Cold on Coumarin-producing Plants . . .	ii, 63
PONTI (UGO). <i>Ajuga Rejva</i> . . .	ii, 63
LEBES (C.). Presence of Aucubin in Different Varieties of <i>Aucuba Japonica</i> . . .	ii, 63
BOURQUELOT (ÉMILE). Occurrence of a Cyanogenetic Glucoside in <i>Linaria Striata</i> . . .	ii, 63
GONIS (A.) and MASORE. Existence of Two New Glucosides, Decomposable by a Ferment, in <i>Primula officinalis</i> . . .	ii, 63
GERBER (C.). Localisation of Proteolytic Ferments in <i>Vasconcellea quercifolia</i> . The Rennet and Spontaneously Coagulable Latex . . .	ii, 64
SIMON (J.). Action of Different Amounts of Copper in the Soil on the Growth of Plants . . .	ii, 64
FRISKE (KURT). Deposition of Nitrogen in Full-grown Animals with Abundant Food . . .	ii, 64
PETTIT (JAMES HARVEY). Soil Analysis . . .	ii, 65

Analytical Chemistry.

KEYES (FREDERICK G.). Improved Method of Collecting Gases from the Mercury Pump . . .	ii, 66
FRAILONG (R.). Automatic Filling Burette . . .	ii, 66
SAND (HENRY J. S.). Apparatus for the Rapid Electro-analytical Separation of Metals . . .	ii, 66
FORMÁNEK (JAROSLAV) and FRANZ PEŮ. Aluminium Dishes and other Appliances in Quantitative Analysis . . .	ii, 67
GOOCH (FRANK A.) and H. L. READ. Electrolytic Estimation of Chlorine in Hydrochloric Acid with the Use of a Silver Anode . . .	ii, 67
MILROY (HUGO). The Beilstein Reaction [for Halogens] . . .	ii, 67
DEHN (WILLIAM M.). Analysis of Mixtures of Halogen Acids. II. . .	ii, 67
ROTHMUND (VICTOR) and A. BURGSTALLER. Estimation of Perchlorates by means of Titanous Salts . . .	ii, 68

	PAGE
WINTERSTEIN (ERNST) and E. HERZFELD. Simple Process for the Estimation of Iodine	ii, 68
PAOLINI (VINCENTO). Estimation of Iodine in Organic Substances	ii, 68
SEIDELL (ATHERTON). Estimation of Iodine in the Thyroid	ii, 69
PELLET (HENRI). Estimation of Sulphur Dioxide and Sulphuric Acid in the Gases of Sulphur Furnaces	ii, 69
BAUDIGNY (HENRI). Estimation of Dithionic Acid and Dithionates	ii, 69
DENSCH. Estimation of Nitrogen in Soil Extracts	ii, 70
ZELLER (T.). Method of Estimating Very Small Amounts of Nitrogen	ii, 70
BERTHOLD (ADOLF). New Distillation Arrangement for Ammonia Estimation	ii, 70
LIECHTI (PAUL) and ERNST RITTER. Estimation of very Small Amounts of Ammonia in Large Quantities of Air	ii, 70
LEO (K.). New Arrangement for the Estimation of Nitric Compounds in Sulphuric Acid	ii, 71
POZZI-ESCOFF (M. EMMANUEL). Reduction of Nitric Nitrogen to Ammonia; New Process for the Estimation of Nitrates	ii, 71
FARCY (L.). Modification of the Grandval and Lajoux Process for the Estimation of Nitrates in Waters Charged with Chlorides	ii, 71
FARCY (L.). Influence of Nitrites on the Estimation of Nitrates by Grandval and Lajoux's Process	ii, 72
FARCY (L.). Influence of Chlorides on the Estimation of Nitrates	ii, 72
LOMBARD (MAURICE). Coloured Substances Produced in Grandval and Lajoux's Reaction	ii, 72
VUAFLEART (L.). Estimation of Mineral Constituents in Vegetable Substances	ii, 72
PELLET (HENRI). Estimation of Mineral Constituents in Vegetable Substances	ii, 72
GUTHRIE (FREDERICK B.) and A. ALEXANDER RAMSAY. Estimation of the Free Acid in Superphosphates	ii, 72
GUENRY (E.) and E. TOUSSAINT. Estimation of Total Phosphoric Acid in Basic Slags and Native Phosphates by the "Citro-mechanic Method"	ii, 73
ROSENHEIM (ARTHUR) and JAKOB PINSKER. Estimation of Hypophosphoric, Phosphorous, and Hypophosphorous Acids in Presence of One Another, and of Phosphoric Acid	ii, 73
BARILLÉ (A.). Apparatus for the Estimation of Carbon Dioxide in Milk	ii, 74
VERWEY (AART). Estimation of Potassium in Potassium Silicates	ii, 74
VOIGT (K.). Estimation of Zinc and Analysis of Zinc Ores	ii, 74
SACHSE (JULIUS F.). The Most Rapid Wet Lead Assay	ii, 75
BECKER (WILH.). Detection of Mercury in Urine	ii, 75
GLASER (FRITZ) and A. ISENBERG. Detection of Mercury in Urine	ii, 75
FERKIN (F. MOLLWO). Electro-analysis of Mercury Compounds with a Gold Cathode	ii, 75
FISCHER (WALDEMAR M.). Estimation of Manganese by Volhard and Wolf's Method	ii, 76
FALOO (FERDINAND). Separation of Manganese and Chromium	ii, 76
BAUDISCH (OSCAR). Quantitative Separations by means of Ammonium "Cupferron" (Nitrosophenylhydroxylamine)	ii, 76
BRIYLLANTS (PIERRE). Rapid Electrolytic Estimation of Cobalt	ii, 77
SCHÖELLER (WALTER) and WALTER SCHRAUTH. Gravimetric Estimation of Chromium; Quantitative Hydrolysis of Sesquioxides	ii, 77
RÖDER (ELISE). Estimation of Titanic Acid in Ilmenite	ii, 78
MINGAYE (JOHN C. H.). Estimation of Thorium in Monazite. Colorimetric Estimation of Small Amounts of Platinum	ii, 78
KOCH (WALDEMAR). Methods for the Quantitative Chemical Analysis of Animal Tissues. I. General Principles	ii, 78
KOCH (WALDEMAR) and SIDNEY A. MANN. Methods for the Quantitative Chemical Analysis of Animal Tissues. II. Collection and Preservation of Material	ii, 79

	PAGE
KOCH (WALDEMAR) and EMMA P. CARR. Methods for the Quantitative Chemical Analysis of Animal Tissues. III. Estimation of the Proximate Constituents	ii, 79
KOCH (WALDEMAR) and FRED. W. URSON. Methods for the Quantitative Chemical Analysis of Animal Tissues. IV. Estimation of the Elements, with Special Reference to Sulphur	ii, 79
OLIVIER (S. C. J.). Volumetric Estimation of Phenol by Lloyd's Method. Tribromophenol Bromide and Hexabromophenoquinone	ii, 80
LITTERSCHEID (FRANZ M.) and J. BORNEMANN. Application of Arsenious Acid in Volumetric Analysis. I.	ii, 80
TISCHTSCHENKO (JOHANN). Simple Distilling Apparatus for the Estimation of Pentosans by Tollens' Method	ii, 81
GRUBE (KARL). [Estimation of Glycogen].	ii, 81
PELLEGER (EDUARD). [Estimation of Glycogen]	ii, 81
SUZUKI (SHIGERU) and EDWIN B. HART. Quantitative Estimation of Lactic Acid in Cheese	ii, 81
JONG (ANNE W. K. DE). Estimation of Cinnamic and Benzoic Acids in Mixtures of the Two Acids	ii, 81
CERVELLO (CARLO). Sodium Phosphotungstate as a Reagent for Uric Acid and other Reducing Substances	ii, 82
KRAUSS (LUDWIG). The Iodine Reaction of Adrenaline	ii, 82
FRERICHS (HEINRICH). Estimation of Morphine in Opium; Extract of Opium and Tincture of Opium	ii, 82
GILY (P. W.), F. G. ALLISON, and HARRY S. GRINDLEY. Estimation of Urea in Urine	ii, 82
LINDSAY (DOROTHY E.). Estimation of Urea, Allantoin, and Amino-acids in Urine	ii, 83
KENNAWAY (ERNEST L.). Estimation of Purine Bases in Urine	ii, 83
PRIMOT (CHARLES). Vanillin as a Test for Antipyrine and Kryogenine; Detection of Antipyrine in Pyrimidine	ii, 83
MENEGHET (L. A.). Attempt to Estimate Indoxyl in Urine	ii, 83
TUNMANN (O.). Cause of the Vanillin Hydrochloric Acid Reaction for Camphor	ii, 84
LESSENG (R. ED.). A Colour Reaction for Gelatin	ii, 84
MCWENNEY (E. J.). The Value of Benzidine for the Detection of Minute Traces of Blood	ii, 84

INDEX OF AUTHORS' NAMES

IN TRANSACTIONS AND ABSTRACTS

A.

Allison, F. G. See P. W. Gill.
Archibald, E. H., ii, 43.
Arrhenius, S., ii, 52.
Aubel, E. van, ii, 28.
Autenrieth, W., and F. Beuttel,
i, 60, 61.
Auwers, K., i, 52.
Auwers, K., and H. Voss, i, 70.

B.

Bach, A., ii, 31.
Badische Anilin- & Soda-Fabrik,
i, 49, 59, 60.
Barcroft, J., and W. O. R. King,
ii, 50.
Bargellini, G., and S. Silvestri,
i, 39.
Barillé, A., ii, 74.
Barkla, C. G., ii, 8.
Barnett, E. de B., TRANS., 63.
Baubigny, H., ii, 69.
Baudisch, O., ii, 78.
Baumann, O. See B. Rassow.
Bauriedel, F. See A. Gutbier.
Bazlen, M., i, 40.
Beburischwilli, M^{me}. T. See J.
Salkind.
Becker, W., ii, 75.
Beckmann, E., and F. Waentig,
ii, 1.
Bernadini, L., and A. Siniscalchi,
ii, 61.
Bernoulli, W. See F. Fichter.
Berthold, A., ii, 70.
Beuttel, F. See W. Autenrieth.
Beveridge, Miss H. H., ii, 25.
Biltz, W., and A. von Vegesack,
ii, 22.
Bloch, L., ii, 32.
Boeters, O. See R. Wolfenstein.
Boisbaudran, P. E. L. de, ii, 3.
Bolin, I. See H. Euler.

Borck, H. See L. Moeser.
Bordas, F., and Tonplain, ii, 57.
Bornemann, J. See F. M. Eitterschcid.
Borsche, W., i, 35.
Borsche, W., and J. C. Titsingh,
i, 65.
Rose, M., ii, 34.
Bottazzi, F., and N. Scalinci, ii, 56.
Bourquetot, E., ii, 63.
Brasch, W., ii, 60.
Braun, J. von, i, 13.
Braun, J. von, and A. Trümpler,
i, 25.
Brauns, R., ii, 9.
Bredt, J., and R. May, i, 32.
Brewster, C. M. See H. A. Torrey.
Brizard, L. See M. de Broglie.
Broglie, M. de, and L. Brizard,
ii, 11.
Brouwer, H. A., ii, 48.
Bruylants, P., ii, 77.
Bucher, J. E., and W. C. Slade,
i, 38.
Buchwitz, J. See H. Staudinger.
Buckmaster, G. A., and J. A. Gardner, ii, 50.
Bühler, L. See A. Edinger.
Bülou, C., i, 81.
Bülou, C., and K. Haas, i, 80.
Buglia, G., and L. Karczag, ii, 52.
Bunzel, H. H. See L. L. Woodruff.
Burgstaller, A. See V. Rothmund.
Burke, C. E. See J. B. Tingle.
Busch, M., i, 75.
Busch, M., and J. Reinhardt, i, 75.
Byk, A., and H. Jaffe, ii, 3.

C.

Cain, J. C. See V. H. Valey.
Callendar, H. L., and H. Moss, ii, 28.
Carlinfanti, E., and M. Levi-Malvano, i, 5, 6.
Carr, E. P. See W. Koch.

Cavalier, J., and E. Cornec, ii, 31.
 Cervello, C., ii, 82.
 Chapman, H. G., and J. M. Petrie,
 i, 82.
 Chemische Fabrik auf Aktien
 (vorm. E. Schering), i, 23.
 Chemische Fabrik von Heyden,
 i, 37.
 Chemische Werke vorm. Dr. Hein-
 rich Byk, i, 31, 81.
 Chieffi, G. See E. Paternò.
 Clarke, R. W. L., and A. Lapworth,
 TRANS., 11.
 Clewer, H. W. B. See F. Tutin.
 Cohen, E., and H. Inouye, ii, 37.
 Colson, A., ii, 34.
 Colwell, H. A., i, 54.
 Cone, L. H. See M. Gomborg.
 Consortium für Elektrochemische
 Industrie. See G. Imbert.
 Cornec, E. See J. Cavalier.
 Cowper, A. D., and G. Tammann,
 ii, 20.
 Cusmano, G., i, 50.
 Cusmano, G. See also L. Francesconi.

D.

Darmois, E., i, 52.
 Darzens, G., i, 63.
 Dautriche, H., ii, 34.
 Dechend, H. von, ii, 2.
 Deetjen, H., ii, 51.
 Dehn, W. M., ii, 67.
 Delépine, M., ii, 34, 44.
 Denison, R. B., ii, 15.
 Densch, ii, 70.
 Dessoullavy, E. See E. Grand-
 mougín.
 Dietrich, M., i, 82.
 Dubreuil, L., ii, 34.

E.

Edinger, A., and L. Bühler, i, 64.
 Ehrenfeld, R., and W. Kuika, ii, 59.
 Ellis, G. W., and J. A. Gardner,
 ii, 58.
 Engler, C., i, 2.
 Engler, C., and O. Rontala, i, 2.
 Ephraim, F., and L. Heymann,
 ii, 37.
 Ephraim, F., and S. Weinberg,
 ii, 41.
 Euler, H., and I. Bolin, i, 84.
 Euler, H., and B. af Ugglas, ii, 25.
 Everest, A. E., ii, 6.

F.

Falkenstein, K. V. von, ii, 27.
 Falco, F., ii, 76.

Farbenfabriken vorm. Friedrich
 Bayer & Co., i, 49, 78.
 Farbwerke vorm. Meister, Lucius
 & Brüning, i, 78, 84.
 Farcy, L., ii, 71, 72.
 Feist, F., i, 7.
 Feist, F., and G. Pomme, i, 9, 39.
 Feist, F., and R. Reuter, i, 9.
 Ferrario, E., and M. Neumann,
 i, 59.
 Fichter, F., and W. Bernoulli,
 i, 20.
 Fichter, F., and O. Walter, i, 29.
 Field, S., ii, 38.
 Fielding, W., ii, 32.
 Fischer, H., i, 22.
 Fisher, W. M., ii, 76.
 Flürscheim, B., TRANS., 84.
 Fock, A., ii, 23.
 Formánek, J., and F. Peč, ii, 67.
 Fouchet, A. See G. Perrier.
 Fox, C. J. J., ii, 29.
 Frailong, F., ii, 66.
 Francesconi, L., and G. Cusmano,
 i, 38.
 Franchimont, A. P. N., i, 4.
 Frank, F., and Schittenhelm
 ii, 52.
 Frankl, T., ii, 59.
 Fredericksz, V. See C. E. Guye.
 Frerichs, H., ii, 82.
 Freund, R. See J. Houben.
 Friend, J. N., ii, 39.
 Friske, K., ii, 64.
 Fritzsche, F., & Co., i, 32.
 Furlong, J. R. See W. Mauchot.

G.

Gardner, J. A. See G. A. Buck-
 master, and G. W. Ellis.
 Garver, M. M., ii, 22.
 Gassmann, T., ii, 57.
 Gasteff, A. See I. Tschugaeff.
 Gaubert, P., i, 62; ii, 4.
 Gerber, C., ii, 64.
 Gill, P. W., F. G. Allison, and H. S.
 Grindley, ii, 82.
 Giomelli, D. See G. Plancher.
 Glaser, F., and A. Isenburg, ii, 75.
 Glikin, W., ii, 58.
 Goettler, M. See R. Pummerer.
 Gomborg, M., and L. H. Cone, with
 O. B. Winter, i, 55.
 Gomeika, F. See A. Stock.
 Gooch, F. A., and H. L. Read, ii, 67.
 Gordin, H. M., i, 62.
 Goris, J. A., and Mascré, ii, 63.
 Grandmougín, E., i, 74.

Grandmougin, E., and E. Dessou-
lavy, i, 72.
Grethe, T. See A. Kötze.
Griffiths, E., ii, 47.
Grindley, H. S. See P. W. Gill.
Gros, O., ii, 51.
Grube, K., ii, 81.
Gry, A. See A. Guyot.
Guerbet, M., i, 52.
Guerry, E., and E. Toussaint,
ii, 73.
Gutbier, A., and F. Bauriedel, i, 12.
Gutbier, A., and K. Maisch, ii, 45.
Guthrie, F. B., and A. A. Ramsay,
ii, 72.
Guye, C. E., and V. Fredericksz,
ii, 21.
Guyot, A., and A. Gry, i, 40.

H.

Haack, H., i, 43.
Haas, K. See C. Bülow.
Haas, P., ii, 57.
Haertel, R. See H. Stobbe.
Hahn, O., and L. Meitner, ii, 8.
Haussen, O., ii, 55.
Hart, E. B. See S. Suzukii.
Hauser, O., and F. Wirth, ii, 47.
Heckel, E., ii, 63.
Heisler, R. See F. Ullmann.
Heller, G., and W. Tischner, i, 37,
64.
Hertzfeld, E. See E. Winterstein.
Heymann, L. See F. Ephraim.
Hill, A. V., ii, 59.
Hill, E. G., and A. P. Sirkar, ii, 27.
Hilpert, S., ii, 39.
Hilpert, S., and E. Kohlmeyer,
ii, 35.
Hinrichs, G. D., ii, 26.
Hinrichsen, F. W., and E. Kindscher,
ii, 62.
Hofmann, K. A., and H. Kirm-
reuther, i, 3, 16.
Hofmann, K. A., H. Wagner, and
A. Zedtwitz, i, 3.
Hosking, R., ii, 20.
Houben, J., R. Freund, and A.
Schottmüller, i, 34.
Howard, H. See F. G. Pope.
Hudson, C. S., and H. S. Paine,
i, 83.

I.

Imbert, G., and Consortium für
Elektrochemische Industrie,
i, 7.
Inoué, K. See E. Cohen.

Isenburg, A. See F. Glaser.
Izar, G., ii, 53.

J.

Jaffe, H. See A. Byk.
Johnson, T. B., i, 69.
Jolkver, Mlle. E., i, 55.
Jones, H. C. See G. F. White.
Jones, L. W., and R. Oesper, i, 13.
Jong, A. W. K. de, ii, 81.
Jorissen, W. P., and N. H. S. van
Reesema, ii, 31.

K.

Kalle & Co., i, 40.
Karandéeff, B., ii, 33.
Karczag, L. See G. Buglia.
Kaya, K., and E. H. Starling, ii, 50.
Kennaway, E. L., ii, 83.
Kessler, S. See H. Rupe.
Keyes, F. G., ii, 66.
Kimura, H., i, 53.
Kindscher, E. See F. W. Hinrichsen.
King, W. O. R. See J. Barcroft.
Kirmreuther, H. See K. A. Hof-
mann.
Kleeman, R. D., ii, 22.
Klobb, T., i, 31.
Koch, A., ii, 60.
Koch, W., ii, 54, 78.
Koch, W., and E. P. Carr, ii, 79.
Koch, W., and S. A. Mann, ii, 79.
Koch, W., and F. W. Upson, ii, 54,
79.
Koenigsberger, J. See J. Weiss.
Kötz, A., and T. Grethe, i, 24.
Kohl, F. G., i, 82.
Kohlmeyer, E. See S. Hilpert.
Kolb, A., ii, 35.
Komppa, G., i, 51.
Krauss, L., ii, 82.
Kruyt, H. R., ii, 28.
Kulka, W. See R. Ehrenfeld.
Kutscher, F., ii, 55.

L.

Laby, T. H., ii, 46.
Lacroix, A., ii, 46, 49.
Laidlaw, P. P., i, 54.
Lapworth, A., and J. R. Partington,
TRANS., 19.
Lapworth, A., and E. Wechsler,
TRANS., 38.
Lapworth, A. See also R. W. L.
Clarke.
Laquer, W., ii, 58.

Lebas, C., ii, 63.
 Leitmeier, H., ii, 49.
 Leo, K., ii, 71.
 Leser, G., i, 48.
 Letsche, E., ii, 52.
 Levene, P. A., and G. M. Meyer, ii, 53.
 Levene, P. A. See also I. Levin.
 Levi-Malvano, M., ii, 37.
 Levi-Malvano, M. See also E. Carlinfant.
 Levin, I., P. A. Levene, and D. D. Manson, ii, 53.
 Levy, P., i, 11.
 Liddle, L. M. See H. L. Wheeler.
 Liebermann, C., and H. Trucksäss, i, 36.
 Liechti, P., and E. Ritter, ii, 70.
 Liesegang, R. E., ii, 64.
 Liljestränd, G., ii, 54.
 Lindsay, D. E., ii, 33.
 Lippmann, E. O. von, i, 55.
 Litterscheid, F. M., and J. Bornemann, ii, 80.
 Locquin, R., i, 10.
 Lombard, M., ii, 72.
 Loring, F. H., ii, 26.
 Losanitsch, S. M., i, 1.
 Lusby, S. G., ii, 10.
 Lyon, E. P., ii, 54.

M.

McBain, J. W., ii, 21.
 McCaughey, W. J., ii, 42.
 McClendon, J. E., ii, 54.
 McWeeney, E. J., ii, 34.
 Madsen, J. P. V., ii, 7.
 Maisch, K. See A. Gutbier.
 Manchot, W., and J. R. Furlong, i, 33.
 Mann, S. A. See W. Koch.
 Mansou, D. D. See I. Levin.
 Marschalk, C., i, 59.
 Mascré. See J. A. Goris.
 May, R. See J. Breit.
 Maze, P., ii, 60.
 Mecklenburgh, W., ii, 41.
 Meigs, E. B., ii, 55.
 Meitner, L. See O. Hahn.
 Mennechet, L. A., ii, 83.
 Merzyng, H., ii, 15.
 Merwin, H. E. See C. Palache.
 Metcalfe, E. P., ii, 11.
 Meulen, H. ter, i, 54.
 Meunier, J., ii, 15.
 Mayer, G. M. See P. A. Levene.
 Meyere, A., ii, 9.
 Micklethwait, Miss F. M. G. See G. T. Morgan.

Milroth, H., ii, 87.
 Mingaye, J. C. H., ii, 78.
 Moeser L., and H. Borck, ii, 36.
 Montagne, P. J., i, 42.
 Morgan, G. T., Miss F. M. G. Micklethwait, and G. T. Whitby, TRANS., 34.
 Morgan, G. T., and J. A. Pickard, TRANS., 48.
 Moruzzi, G., i, 81.
 Moss, H. See H. L. Callendar.
 Muller, J. A., ii, 24.

N.

Neumann, M. See E. Ferrario.
 Noyes, W. A., ii, 27.

O.

Obermiller, J., i, 28.
 Oesper, R. See L. W. Jones.
 Olivari, F., ii, 18.
 Olivier, S. C. J., ii, 80.
 Osterhout, W. J. V., ii, 62.

P.

Padoa, M., ii, 6.
 Paine, H. S. See C. S. Hudson.
 Palache, C., and H. E. Merwin, ii, 47.
 Paladino, R., ii, 50.
 Paolini, V., ii, 68.
 Parnass, J., i, 4.
 Partington, J. R. See A. Lapworth.
 Paschen, F., ii, 3.
 Paternò, E., and G. Chieffi, i, 41.
 Peč, F. See J. Formánek.
 Pellet, H., ii, 69, 72.
 Perkin, F. M., ii, 75.
 Perrier, G., and A. Fouchet, i, 54.
 Petrie, J. M. See H. G. Chapman.
 Pettit, J. H., ii, 65.
 Pilüger, E., ii, 81.
 Piccard, J., i, 66, 67.
 Pickard, J. A. See G. T. Morgan.
 Pilipenko, P. P., ii, 45, 48.
 Pinsker, J. See A. Rosenheim.
 Piutti, A., i, 22.
 Plancher, G., and D. Giunelli, i, 63.
 Pochettino, A., ii, 5.
 Pollock, J. A., ii, 11.
 Pomme, G. See F. Feist.
 Ponti, U., ii, 63.
 Pope, F. G., and H. Howard, TRANS., 78.

Pozzi-Escot, M. E., ii, 71.
 Prideaux, E. B. R., ii, 12.
 Primot, C., ii, 83.
 Provenzal, G. See R. Spallino.
 Pummerer, R., and M. Goettler,
 i, 77.
 Purvis, J. E., ii, 3.

Q.

Quagliariello, G., ii, 56.

R.

Rakusin, M., ii, 45.
 Ramberg, L., i, 4.
 Ramsay, A. A. See F. B. Guthrie.
 Rassow, B., and O. Baumann, i, 79.
 Read, H. L. See F. A. Gooch.
 Reesema, N. H. S. van. See W. P.
 Jorissen.
 Reichel, H., ii, 61.
 Reinhardt, J. See M. Busch.
 Reinhold, B. See E. H. Riesenfeld.
 Rengade, E., ii, 16, 17.
 Reuter, R. See F. Feist.
 Richards, T. W., ii, 19.
 Richarz, F., ii, 27.
 Riesenfeld, E. H., and B. Reinhold,
 ii, 14, 33.
 Riesenfeld, E. H., and F. Seemann,
 ii, 39.
 Ritter, E. See P. Liechti.
 Robinson, W. O., and W. H. Wagga-
 man, ii, 37.
 Röer, E., ii, 78.
 Rolla, L., ii, 19.
 Romburgh, P. van, i, 19.
 Rosenheim, A., i, 13.
 Rosenheim, A., and J. Pinsker,
 ii, 73.
 Rosenmund, K. W., i, 67.
 Rothmund, V., and A. Burgstaller,
 ii, 68.
 Rottala, O. See C. Engler.
 Ruhland, W., ii, 63.
 Rupe, H., and S. Kessler, i, 15.
 Rupe, H., and K. G. Thiess, with A.
 Wetter, i, 71.

S.

Sacerdote, P., ii, 8.
 Sacher, J. F., ii, 75.
 Salkind, J., and Mdme. T. Bebur-
 ischwili, i, 11.
 Salkowski, E., ii, 55.
 Sand, H. J. S., ii, 66.
 Sarthou, J., ii, 57.
 Sato, T., ii, 56, 58.

Scalinci, N. See F. Bottazzi.
 Schaefer, O. C., and H. Schlundt,
 ii, 12.
 Schenck, M., i, 10.
 Schittenhelm, A., ii, 52.
 Schittenhelm, A., and K. Wiener,
 ii, 52.
 Schittenhelm, A. See also F. Frank.
 Schlundt, H. See O. C. Schaefer.
 Schmidt, H. W., ii, 7.
 Schmidt, J., and H. Stützel, i, 29.
 Schmidt-Nielsen, S., and S. Schmidt-
 Nielsen, i, 83.
 Schmidt-Nielsen, S. See S. Schmidt-
 Nielsen.
 Schoeller, W., and W. Schrauth,
 ii, 77.
 Schossberger, E. See F. W. Semmler.
 Schottmüller, A. See J. Houben.
 Schrauth, W. See W. Schoeller.
 Schulze, E., and G. Trier, i, 62.
 Seemann, F. See E. H. Riesenfeld.
 Seidell, A., ii, 69.
 Semmler, F. W., and E. Schoss-
 berger, i, 53.
 Sanderens, J. B., i, 11.
 Sarra, A., ii, 48.
 Seydel, S. See H. Stobbe.
 Silvestri, S. See G. Bargellini.
 Simon, J., ii, 64.
 Stiscalchi, A. See L. Bernadini.
 Sirkar, A. P. See E. G. Hill.
 Slade, W. C. See J. E. Bucher.
 Smits, A., ii, 24.
 Soddy, F., ii, 10.
 Söll, J., and A. Stutzer, i, 14.
 Spallino R., and G. Provenzal, i, 33.
 Spring, W., i, 6.
 Starling, E. H. See R. Kaya.
 Staudinger, H., and J. Buchwitz,
 i, 46.
 Stobbe, H., i, 43.
 Stobbe, H., and R. Haertel, i, 43.
 Stobbe, H., R. Haertel, and S.
 Seydel, ii, 4.
 Stobbe, H., and S. Seydel, i, 45.
 Stock, A., and F. Gomolka, ii, 30.
 Stoltzenberg H., ii, 17.
 Strutt, R. J., ii, 9.
 Stützel, H. See J. Schmidt.
 Stutzer, A. See J. Söll.
 Suzukii, S., and E. B. Hart, ii, 81.
 Svedberg, T., ii, 23.
 Szilárd, R., ii, 7.

T.

Takemura, M., i, 82.
 Tammann, G., ii, 17.
 Tammann, G. See also A. D.
 Cowper.

Tarbouriech, P. J., i, 32.
 Taylor, A. E., i, 82.
 Thiess, K. G. See H. Rupe.
 Thomas, C., ii, 42.
 Thunberg, T., ii, 54.
 Timmermans, J., ii, 19.
 Tingle, J. B., and C. E. Burke, i, 21.
 Tischner, W. See G. Heller.
 Tischtschenko, J., ii, 81.
 Titsingh, J. C. See W. Borsche.
 Torrey, H. A., and C. M. Brewster,
 i, 47.
 Touplain. See F. Bordas.
 Toussaint, E. See E. Guerry.
 Fraube, I., ii, 20.
 Trautz, M., ii, 24.
 Treboux, O., ii, 61.
 Trier, G. See E. Schulze.
 Trucksäss, H. See C. Liebermann.
 Trumpler, A. See J. von Braun.
 Tschugaeff, L., and A. Gasteff,
 i, 31.
 Tunmann, O., ii, 84.
 Tutin, F., and H. W. B. Clewer,
 TRANS., 1.

U.

Ugglass, B. af. See H. Euler.
 Ullmann, F., and R. Heisler, i, 74.
 Ultée, A. J., i, 14.
 Upson, F. W. See W. Koch.
 Urazoff, G. G., ii, 43.
 Usher, F. L., TRANS., 66.

V.

Vavon, G., i, 52.
 Vegesack, A. von. See W. Biltz.
 Veley, V. H., with J. C. Cain, ii, 25.
 Veley, V. H., and A. D. Waller,
 ii, 55.
 Verwey, A., ii, 74.
 Voigt, K., ii, 74.
 Voss, H. See K. Auwers.
 Voswinckel, H., i, 42.
 Voswinckel, H., and F. de Weerth,
 i, 49.
 Vouk, V., ii, 62.

Vries, O. de, i, 29.
 Vuahart, L., ii, 72.

W.

Waentig, P. See E. Beckmann.
 Waggaman, W. H. See W. O.
 Robinson.
 Wagner, H. See K. A. Hofmann.
 Waller, A. D. See V. H. Veley.
 Walter, O. See F. Fichter.
 Warburg, E., ii, 6.
 Waterman, N., ii, 59.
 Wechsler, E. See A. Lapworth.
 Weerth, F. de. See H. Voswinckel.
 Wegscheider, R., i, 6.
 Wehmer, C., ii, 61.
 Weinberg, S. See F. Ephraim.
 Weiss, J., and J. Koenigsberger,
 ii, 15.
 Wenk, W., ii, 23.
 Werner, A., i, 20.
 Wetter, A. See H. Rupe.
 Wheeler, H. L., and L. M. Liddle,
 i, 17, 19.
 Whiddington, R., ii, 6.
 Whitby, G. S. See G. T. Morgan.
 White, G. F., and H. C. Jones, ii, 13.
 Wiener, K. See A. Schittenhelm.
 Wilkinson, J. A., ii, 5.
 Winter, O. B. See M. Gomborg.
 Winterstein, E., and E. Herzfeld,
 ii, 68.
 Wirth, F. See O. Hauser.
 Wohlleben, W. J., i, 27.
 Wollfenstein, R., and O. Boeters,
 i, 27.
 Woodruff, L. L., and H. H. Bunzel,
 ii, 59.

Y.

Young, W. J., i, 12.

Z.

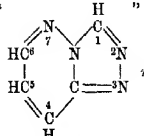
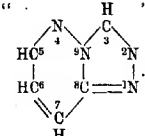
Zedtwitz, A. See K. A. Hofmann.
 Zeller, T., ii, 70.

ERRATA.

VOL. XCVI (ABSTR., 1909).

PART I.

Page Line

		“		”	“		”
614	9*	for		read			
614	8*	„	“ 4 : 6-Dimethyl-2 : 3 : 7 : 8-tetrahydro-1,2,4-diazepine ”	read	“ 5 : 7-Dimethyl-1 : 2 : 4 : 9-benzotetrazole. ”		
615	3	„	“ 4 : 5 : 6-Trimethyl-2 : 3 : 7 : 8-tetrahydro-1,2,4-diazepine ”	read	“ 5 : 6 : 7-Trimethyl-1 : 2 : 4 : 9-benzotetrazole. ”		
615	7, 8	„	“ 4-phenyl-6-methyl-2 : 3 : 7 : 8-tetrahydro-1,2,4-diazepine ”	read	“ 7-phenyl-5-methyl-1 : 2 : 4 : 9-benzotetrazole. ”		
615	21	„	“ 4-Hydroxy-6-methyl-2 : 3 : 7 : 8-tetrahydro-1,2,4-diazepine ”	read	“ 7-Hydroxy-5-methyl-1 : 2 : 4 : 9-benzotetrazole. ”		
615	11*	„	“ 4-Hydroxy-5 : 6-dimethyl-2 : 3 : 7 : 8-tetrahydro-1,2,4-diazepine ”	read	“ 7-Hydroxy-5 : 6-dimethyl-1 : 2 : 4 : 9-benzotetrazole. ”		
615	4*	„	“ 4-Hydroxy-6-phenyl-2 : 3 : 7 : 8-tetrahydro-1,2,4-diazepine ”	read	“ 7-Hydroxy-5-phenyl-1 : 2 : 4 : 9-benzotetrazole. ”		
616	7	„	“ hydroxyphenyldiazepine ”	read	“ hydroxyphenylbenzotetrazole. ”		

PART II.

527 3* „ “GEORGES” read “GABRIEL.”

* From bottom.

JOURNAL
OF
THE CHEMICAL SOCIETY.

TRANSACTIONS.

I.—*The Constituents of Rumex Ecklonianus.*

By FRANK TUTIN and HUBERT WILLIAM BENTLEY CLEWER.

Rumex Ecklonianus, Meisner (*N. O. Polygonaceae*), is an herb indigenous to South Africa, where it is reputed to possess medicinal properties. It is referred to in "A Contribution to South African Materia Medica," by Andrew Smith, 1895, p. 107, and also in the Transactions of the South African Philosophical Society, 18, part 2, p. 216. A botanical description of the plant will be found in *Linnaea*, 1840, 14, 493.

The investigation of the above-mentioned plant has resulted in the isolation of a number of crystalline substances, some of which are anthraquinone derivatives, such as have previously been isolated from other members of the *Polygonaceae*. A complete summary of the results obtained will be found at the end of this paper.

EXPERIMENTAL.

The material employed consisted of the entire overground portions of the above-mentioned *Rumex Ecklonianus*, collected at the time of flowering, and was received through the kindness of Mr. G. E. Oliver, of East London, South Africa, who stated that it occurred as a common weed on the banks of rivulets and in

marshy places. It had, however, been incorrectly designated by Mr. Oliver as *Polygonum tomentosum*, var. *glabrum*, but its identity as the first-mentioned plant was ascertained by Mr. E. M. Holmes, F.L.S., who had kindly compared it with specimens in the herbarium at Kew.

A portion (50 grams) of the finely-powdered, dried herb was successively extracted in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 110°, were obtained:

Petroleum (b. p. 35–50°) extracted	0.77 gram	=	1.54 per cent.
Ether	0.51	=	1.02 "
Chloroform	0.69	=	1.38 "
Ethyl acetate	0.69	=	1.38 "
Alcohol	4.07	=	8.14 "

Total = 6.73 grams or 13.46 per cent.

After having ascertained by a preliminary experiment that no alkaloid was present, a quantity (11.733 kilograms) of the dried and ground herb was completely extracted by percolation with cold alcohol. The greater part of the alcohol was removed from the resulting extract, when 1.8 kilograms of a thin extract, containing a quantity of black, tarry matter, were obtained.

The entire amount of the above-mentioned extract was mixed with water and distilled with steam until volatile products ceased to be removed. The distillate, which contained a small amount of oil, and also some solid, was extracted with ether, the resulting ethereal liquid being shaken with a solution of sodium carbonate. This treatment removed from the ether a small amount of a substance, which, after being twice crystallised from ethyl acetate, formed yellowish-brown, slender prisms, melting at 159°. This substance dissolved in concentrated sulphuric acid, yielding a golden-yellow liquid, and its alcoholic solution gave with ferric chloride a green colour, which gradually changed to reddish-brown, but the amount obtained was not sufficient for its further examination. The ethereal liquid which had been treated with sodium carbonate yielded, on evaporation, a small amount of an essential oil, which possessed a dark green colour and an odour closely resembling that of the rhubarb of the Pharmacopœias.

The contents of the distillation flask then consisted of a quantity of a dark green resin (A), together with a dark-coloured aqueous liquid. These products were separated while still hot, when, on allowing the liquid to cool, a quantity of a brown resin (B) was deposited. The latter was likewise separated from the aqueous liquid (C).

Examination of the Green Resin (A).

The green resin, which formed a viscid mass, and amounted to 346 grams, was mixed with purified sawdust, and the dried mixture extracted successively in a large Soxhlet apparatus with light petroleum, ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Green Resin.

This extract, after the complete removal of the solvent, amounted to about 100 grams. It was dissolved in 1.5 litres of ether, and the ethereal liquid shaken with several successive portions of a 5 per cent. solution of ammonium carbonate. During shaking with the first portion of ammonium carbonate solution, a quantity of crystalline substance separated from the ether. This was collected, and its examination will subsequently be described. The further treatment with ammonium carbonate resulted in the formation of inseparable emulsions, owing to the gradual formation of a product in the form of an amorphous, black powder. The deposition of the latter was effected by removing the ether from the emulsion by passing air through the mixture, after which the solid was collected, but no crystalline substance could be obtained from it. The combined alkaline liquids were acidified, when a small amount of a product was precipitated in the form of a yellowish-brown powder. This was crystallised several times from ethyl acetate, and finally from ether, when it was obtained in long, deep golden-coloured needles, melting at 176° , but the amount was too small for analysis.

Isolation of Emodin Monomethyl Ether.

The previously-mentioned crystalline product, which separated from the ether during the first extraction with alkali, was re-crystallised several times from ethyl acetate, with the use of animal charcoal, when it formed handsome, golden-coloured plates, melting at 197° :

0.1257 gave 0.3116 CO_2 and 0.0493 H_2O . $\text{C} = 67.6$; $\text{H} = 4.4$.

$\text{C}_{16}\text{H}_{12}\text{O}_5$ requires $\text{C} = 67.6$; $\text{H} = 4.2$ per cent.

This substance proved to be emodin monomethyl ether, which has previously been obtained by Perkin and Hummel from *Ventilago madraspatana* (Trans., 1894, **65**, 932). Its identity was confirmed by the preparation of its acetyl derivative, which formed long, pale yellow needles, melting at 185 – 186° . Emodin was methylated by Jowett and Potter (Trans., 1903, **77**, 1330), who obtained a monomethyl ether, melting at 200° . They con-

sidered, however, that the ether prepared by them differed from the naturally occurring compound, inasmuch as it yielded an acetyl derivative melting at 157° . A specimen of the emodin monomethyl ether prepared by Jowett and Potter being available to us, we compared it directly with the analogous compound obtained from *Rumex Ecklonianus*, when the two substances were found to be identical. A quantity of the synthetical compound was then acetylated, when the above-described acetyl derivative, melting at $185\text{--}186^{\circ}$, was obtained. It is evident, therefore, that the natural and synthetical emodin monomethyl ethers are identical, and the low melting point found by Jowett and Potter for the acetyl derivative of the synthetical compound must be attributed to incomplete acetylation. In this connexion it may be noted that the conversion of emodin monomethyl ether into its acetyl derivative takes place only very slowly, unless a powerful condensing agent, such as camphorsulphonic acid, is employed. In order further to confirm the identity of the natural and synthetical compounds, emodin, which was subsequently isolated in the present investigation, was methylated, whereby a monomethyl ether was obtained, which proved to be identical with that occurring in the plant.

The ethereal liquid, which had been extracted with ammonium carbonate, was then shaken with several successive portions of aqueous potassium carbonate. This caused the formation of emulsions, which, after standing for some time, were separated from the ether and repeatedly washed with this solvent. In order to ensure the complete freedom of the potassium carbonate extract from substances insoluble in this alkali, the total quantity of emulsion was acidified and the product extracted with much ether, after which it was again treated with potassium carbonate, the emulsion being separated from the ether and washed as before. This process was twice repeated. The alkaline emulsions were finally acidified, and the product extracted with ether, after which the ethereal liquid was concentrated to a small bulk and treated with light petroleum. This caused the precipitation of a quantity of the previously-mentioned black, amorphous powder, which was removed by filtration. The clear, dark green filtrate was concentrated to a small bulk, when a quantity of a substance separated after some time. This was collected and recrystallised several times from glacial acetic acid, after which it formed colourless leaflets, melting at $56\text{--}60^{\circ}$. On analysis it was found to consist essentially of palmitic acid.

The original filtrate from this product evidently contained further

quantities of fatty acids, and in order to separate these from any phenolic substances which might be present, the entire product was esterified by means of alcohol and sulphuric acid. The material was then dissolved in ether and washed with water, after which it was shaken with potassium carbonate solution. The first treatment with this alkali removed only a quantity of tarry product, but the alkaline extracts subsequently obtained were deep red in colour, and, on acidification, yielded some emodin, which was afterwards obtained in larger amount. Extraction of the ethereal solution of the esters with potassium hydroxide removed only a small amount of impure emodin monomethyl ether, but on subsequently washing it with water a large amount of chlorophyll was removed.

Isolation of a Phytosterol, $C_{20}H_{34}O$.

The ethereal solution of the esters which had been freed from substances soluble in alkalis was evaporated, and the residue distilled under diminished pressure. When the greater part of the product had passed over, it was observed that the residue in the distillation flask possessed a very high boiling point, and tended to become solid. The distillation was therefore stopped, and the undistilled material boiled with alcoholic potash. After removing the greater part of the alcohol, water was added, and the mixture extracted with ether. In this way, a substance was obtained which crystallised from a mixture of ethyl acetate and dilute alcohol in colourless plates, melting at 134° :

0.1024, on drying at 110° , lost 0.0048 H_2O . $H_2O = 4.7$.

0.0976 gave 0.2962 CO_2 and 0.1032 H_2O . $C = 82.8$; $H = 11.7$.

$C_{20}H_{34}O, H_2O$ requires $H_2O = 5.8$ per cent.

$C_{20}H_{34}O$ requires $C = 82.8$; $H = 11.7$ per cent.

This phytosterol appeared to be identical with rhamnol, an alcohol which was first isolated by Power and Lees from *Kô-sam* fruits (*Year Book of Pharmacy*, 1903, 503), and also occurs in the bark of *Rhamnus purshiana* (Jowett, *Proc. Amer. Pharm. Assoc.*, 1904, 299). It is evident, however, that this alcohol must have occurred in the plant in the form of an acid ester, or analogous compound, since the product from which it was obtained was entirely soluble in alkali carbonates.

The esters of the fatty acids, which had been separated from the above-described alcohol by distillation, were examined in connexion with the acids subsequently obtained from the neutral portion of the petroleum extract of the resin.

Isolation of Chrysophanic Acid.

The original ethereal solution of the petroleum extract of the resin, which had been extracted with ammonium and potassium carbonates, was shaken with a solution of potassium hydroxide. This yielded a deep red liquid, which, on acidification, gave a quantity of a yellow powder. The latter was mixed with the material contained in the mother liquors previously obtained during the purification of the emodin monomethyl ether, and the entire product fractionally crystallised many times from a mixture of ethyl acetate and alcohol. A substance was thus obtained which crystallised in deep golden-coloured spangles, melting at 190° :

0.0807 gave 0.2097 CO_2 and 0.0307 H_2O . $\text{C}=70.9$; $\text{H}=4.2$.

$\text{C}_{15}\text{H}_{10}\text{O}_4$ requires $\text{C}=70.9$; $\text{H}=3.9$ per cent.

This substance was thus identified as chrysophanic acid, and its identity was confirmed by the preparation of its acetyl derivative. The latter compound formed bright yellow leaflets, melting at $204-205^{\circ}$.

Dimethyl ether of chrysophanic acid.—It was shown by Jowett and Potter (*loc. cit.*) that chrysophanic acid was not methylated when heated in a sealed tube at 100° with sodium and methyl iodide in the presence of methyl alcohol. It has now been found, however, that methylation does occur if the latter liquid is absent.

Chrysophanic acid (0.2 gram) was dissolved in absolute alcohol, and a solution of 0.04 gram of sodium in the same solvent added. The liquid was then concentrated, when the sodium derivative, which had separated in the form of small, violet-coloured needles, was rapidly collected and dried. This was then heated with dry methyl iodide in a sealed tube at 100° for six hours. After removing the excess of methyl iodide, the residue was acidified with acetic acid and dissolved in chloroform, the solution thus obtained being freed from unchanged chrysophanic acid by means of potassium hydroxide. On removing the solvent, a product was obtained which crystallised from ethyl acetate in yellow prisms, melting at 190° :

0.0956 gave 0.2520 CO_2 and 0.0430 H_2O . $\text{C}=71.9$; $\text{H}=5.0$.

$\text{C}_{17}\text{H}_{14}\text{O}_4$ requires $\text{C}=72.3$; $\text{H}=5.0$ per cent.

Chrysophanic acid dimethyl ether dissolves in cold concentrated sulphuric acid, giving a deep purple solution. It is insoluble in cold aqueous potassium hydroxide, but on boiling with this reagent it slowly dissolves, yielding a red solution, thus indicating that at least one methyl group is gradually removed by the alkali.

The product contained in the mother liquors obtained during

the purification of the chrysophanic acid was found to consist entirely of a mixture of the latter with emodin monomethyl ether, since, after heating at 160° with concentrated sulphuric acid, it was resolved into emodin and chrysophanic acid. The total amount of anthraquinone derivatives present in the petroleum extract of the green resin was 4.5 grams.

Isolation of Ceryl Alcohol.

The ethereal solution of the neutral portion of the petroleum extract of the green resin was evaporated, and the residue boiled with an excess of alcoholic potash. After removing the greater part of the alcohol, water was added, and the unsaponifiable matter extracted with ether. The product so obtained was fractionally distilled under diminished pressure. The portion boiling below $305^{\circ}/20$ mm. was an unsaturated, oily liquid, but the fraction distilling above this temperature gradually solidified. This was crystallised several times from absolute alcohol, when colourless leaflets, melting at 75° , were obtained:

0.0821 gave 0.2466 CO_2 and 0.1031 H_2O . $\text{C} = 81.9$; $\text{H} = 14.0$.

$\text{C}_{27}\text{H}_{56}\text{O}$ requires $\text{C} = 81.8$; $\text{H} = 14.1$ per cent.

This substance therefore appeared to be ceryl alcohol.

Some phytosterol was present in the mother liquors from the above-described product, but no pure substance could be isolated from them.

Isolation of Ipuranol, $\text{C}_{25}\text{H}_{38}\text{O}_2(\text{OH})_2$.

The alkaline liquid, from which the unsaponifiable matter had been removed by means of ether, was acidified and distilled with steam, but no volatile acids were obtained. The contents of the distillation flask were then shaken with ether, when a small amount of flocculent matter collected in the lower portion of the ethereal layer. This was separated by filtration, and purified by crystallisation from dilute pyridine with the use of animal charcoal. It was thus obtained as a colourless, minutely crystalline product, which melted at $285\text{--}290^{\circ}$, and yielded an acetyl derivative crystallising in leaflets, which melted at 162° . A comparison of this acetyl derivative with that obtained from ipuranol (Trans., 1908, 93, 907) rendered it evident that the two substances were identical.

Identification of the Fatty Acids.

The ethereal solution of the fatty acids from which the above-described ipuranol had been separated was evaporated to a small bulk, and treated with a large volume of light petroleum. This

caused the precipitation of a considerable amount of a black, amorphous powder, which was removed by filtration. The fatty acids contained in the filtrate were then distilled under diminished pressure, after which the saturated and unsaturated constituents were separated by means of their lead salts. A quantity (6 grams) of a mixture of palmitic and stearic acids was thus obtained, which melted at 55–56°, together with 18 grams of liquid acids, which had an iodine value of 173.9.

The previously-mentioned ethyl esters of the acids which had occurred in the plant in the free state were then hydrolysed, and the resulting mixture of acids similarly separated into its solid and liquid components, which amounted to 2 grams and 20 grams respectively. The latter product had an iodine value of 169.5. In order to ascertain the constituents of these mixtures of unsaturated acids, 15 grams of both the free and combined liquid acids were together oxidised with potassium permanganate in the manner described by Lewkowitsch (*Chemical Technology and Analysis of Oils, Fats, and Waxes*, 1904, 1, 360). This resulted in the formation of isolinic acid and di- and tetra-hydroxystearic acids, the last-mentioned compound predominating. The unsaturated acids therefore consisted of linolic acid, together with smaller amounts of isolinolenic and oleic acids.

Ethereal Extract of the Green Resin.

Isolation of Emodin and Kaempferol.

This extract amounted to 62 grams. A portion of it (about 6 grams) was very sparingly soluble in ether, and formed a nearly black, amorphous powder, from which nothing could be isolated. The ethereal solution of the more readily soluble portion of the extract was first treated with a solution of ammonium carbonate, but this removed only resinous products, from which nothing crystalline could be separated. The ethereal liquid was then shaken with six successive portions of aqueous potassium carbonate. The first of these operations caused the precipitation of a small amount of black tarry matter, which yielded nothing crystalline, but the aqueous, alkaline liquids subsequently obtained possessed a deep red colour, and, on acidification, yielded a brown powder. This was collected and submitted to a number of fractional crystallisations from glacial acetic acid, when it was ultimately resolved into two products. One of these formed pale yellow, acicular crystals, melting at 276°:

0.0638 gave 0.1586 CO_2 and 0.0227 H_2O . C=62.9; H=3.7.

$\text{C}_{11}\text{H}_{10}\text{O}_6$ requires C=62.9; H=3.5 per cent.

Although the total amount of the above-described product did not exceed 0.15 gram, its identity as kaempferol (1:3:4-trihydroxyflavonol) was positively confirmed by the characteristic behaviour of its acetyl derivative. The latter compound, prepared in the usual manner, and recrystallised from methyl alcohol, first melted at 121° , then resolidified, and finally fused at 182° (compare Perkin, Trans., 1902, 81, 587).

The second crystalline compound obtained from the potassium carbonate extract of the portion of the resin soluble in ether formed dark red needles, melting at 255° , and amounted to 1 gram: 0.0803 gave 0.1954 CO_2 and 0.0281 H_2O . $\text{C}=66.4$; $\text{H}=3.9$.

$\text{C}_{15}\text{H}_8\text{O}_6$ requires $\text{C}=66.7$; $\text{H}=3.7$ per cent.

The identity of this substance with emodin was confirmed by the preparation of its acetyl derivative, which formed golden-yellow needles, melting at $190-191^{\circ}$.

Subsequent treatment of the original ethereal liquid with aqueous potassium hydroxide removed about 4 grams of a mixture of chrysophanic acid and emodin monomethyl ether, after which the ethereal liquid contained only small amounts of green resin.

Chloroform, Ethyl Acetate, and Alcoholic Extracts of the Green Resin.

The chloroform, ethyl acetate, and alcoholic extracts of the resin amounted to 60, 50, and 70 grams respectively. They were all examined in an exhaustive manner, but were found to consist entirely of resins.

Examination of the Brown Resin (B).

This resin, which was soluble in hot water, but again separated on allowing its solution to cool, was thoroughly examined, but nothing definite could be isolated from it. In order to ascertain whether it contained a glucoside, a portion of it was submitted to the action of 5 per cent. aqueous sulphuric acid, but no sugar was formed by this treatment.

Examination of the Aqueous Liquid (C).

The original dark-coloured aqueous liquid (C) was evaporated under diminished pressure to about 1.5 litres, and extracted many times with ether. The ethereal liquid thus obtained was treated first with a solution of ammonium carbonate, then with sodium carbonate, and finally with aqueous sodium hydroxide. The first of these reagents removed a small amount of a product in the form of a gum-like mass, but on extracting the latter with suc-

cessive portions of boiling benzene, evidence was obtained of the existence in it of several crystalline substances. The amounts were so small, however, that none of these could be isolated in a state of purity. The sodium carbonate extracts yielded a small amount of emodin, and a little of a compound which formed pale yellow, acicular crystals, melting at 247° . The latter compound appeared to be pure, but the amount was too small for analysis. It dissolved in alkalis, yielding a solution which was at first colourless, but darkened on exposure to the air, whilst its solution in concentrated sulphuric acid exhibited a purple-blue fluorescence. The material removed from the original ethereal liquid by means of alkali hydroxide yielded nothing definite.

In order to search for a glucoside in the aqueous liquid, the latter was further evaporated under diminished pressure, and the resulting syrup submitted to a prolonged process of extraction with absolute alcohol, followed by ethyl acetate, in a manner similar to that successfully employed by Power and Moore for the isolation of *l*-mandelonitrile glucoside from the bark of *Prunus serotina* (Trans., 1909, 95, 257). During this process 80 grams of potassium chloride and a considerable amount of ammonium chloride separated, but no indication could be obtained of the presence of a glucoside. The viscid syrup, representing the organic constituents of the aqueous liquid which were insoluble in ethyl acetate, was then dissolved in water, and treated with an excess of a solution of basic lead acetate. This caused a voluminous precipitate, from which nothing definite could be isolated. The filtrate from the basic lead acetate precipitate was deprived of lead by means of hydrogen sulphide, and concentrated, under diminished pressure. The liquid so obtained contained a small amount of a sugar, which yielded *d*-phenylglucosazone (m. p. 214°), and, on keeping for some time, a considerable quantity of ammonium nitrate was deposited, but no other crystalline substance could be obtained from it.

Summary.

The results of the preceding investigation of *Rumex Ecklonianus*, Meisner, may be summarised as follows.

An alcoholic extract of the herb, when distilled with steam, yielded a trace of a substance which formed yellow prisms, melting at 159° , together with a small amount of essential oil. The non-volatile constituents of the extract consisted largely of brown, resinous matter and a product which slowly formed a black, amorphous powder, but the following definite substances were also obtained: Ceryl alcohol; a phytosterol, $C_{27}H_{54}O$, apparently

identical with rhamnol; palmitic, stearic, oleic, linolic, and *iso*-linolenic acids; a small amount of ipuranol, $C_{28}H_{38}O_2(OH)_2$; kaempferol; chrysophanic acid; emodin; and emodin monomethyl ether; together with traces of other crystalline substances and large amounts of inorganic salts. A sugar which yielded *d*-phenyl-glucosazone was also present in small amount, but no evidence could be obtained of the presence of a glucoside. The emodin monomethyl ether which was isolated was identical with that obtained by Perkin and Hummel from *Ventilago madraspatana* (Trans., 1894, 65, 932), and with that prepared synthetically by Jowett and Potter (Trans., 1903, 77, 1330). The dimethyl ether of chrysophanic acid was prepared, and obtained in yellow prisms, melting at 191° .

The extract from this plant, like many other products containing anthraquinone derivatives, was found to possess a mild purgative action.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

II.—Cyanocarone.

By REGINALD WILLIAM LANE CLARKE and ARTHUR LAPWORTH.

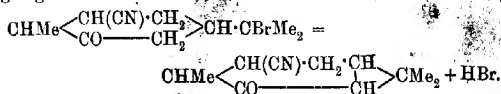
ALTHOUGH carvone and its dihydro-derivative only differ inasmuch as the six-carbon ring in the former contains an ethylenic linking, the products which their hydrobromides yield by loss of hydrogen bromide under the influence of alkalis are quite different in structure; as carvone contains a three-carbon and a six-carbon ring, whilst neither nucleus is present in eucarvone, which appears to contain only one seven-membered ring (Wallach, *Annalen*, 1905, 339, 94, *et seq.*).

The explanation of the formation of eucarvone which most naturally suggests itself is the one indicated by Wallach, namely, that in the first stage of the action of potassium hydroxide on carvone hydrobromide, halogen hydride is removed in the same manner as in the case of dihydrocarvone hydrobromide, but that the molecule of the resulting compound is less stable than that of carvone, owing to the additional strain produced by the ethylenic linking, and consequently the cyclopropane ring is at once resolved, but between the two carbon atoms which previously formed part of the six-ring of the carvone hydrobromide; hitherto, however, no direct evidence confirming this idea has been forthcoming. Had it

been possible to remove two hydrogen atoms from carone, or to separate two groups from adjacent carbon atoms in a substitution product of carone, in such a way as to produce an ethylenic linking at the position where this is found in the hypothetical intermediate compound, it would have been possible to ascertain whether this at once resulted in the formation of eucarvone, and thus to confirm the view referred to, but no substituted derivatives of carone yet appear to have been obtained either by direct substitution or by preparing them from substituted dihydrocarvones.

The investigation of the action of alkalis on cyanodihydrocarvone seemed likely to lead to the formation of such a substituted carvone, and since it has been shown by one of us that β -cyano-derivatives of ketones are frequently convertible into $\alpha\beta$ -unsaturated ketones by the action of alkalis in presence of ferrous hydroxide, a possible mode of attacking this question was promised.

After many unsuccessful attempts, pure cyanocarone was obtained by a method similar to that used in preparing carone from dihydrocarvone, and under certain conditions it was found that cyanodihydrocarvone hydrobromide might be converted nearly quantitatively into the new substance, only traces of cyanodihydrocarvone being regenerated:

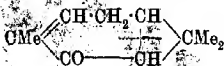


A mixture of isodynamic forms is doubtless produced in the first instance, but in presence of the alkali, which acts as equilibrator, these, during the process of solidification, change with such ease that only one isomeride remains, the equilibrium mixture being saturated with respect to one form.

The product, when nearly pure, crystallises in massive, transparent forms, and has the properties which it might be anticipated a substance having the above constitution would possess. By the action of mineral acids, the *cyclopropane* complex is attacked in all cases before the cyano-group is affected, and with halogen hydrides the first product appears invariably to be the compound of the acid with cyanodihydrocarvone, the reaction above represented taking place in the reverse sense.

The nitrile is saturated in character, and is attacked by cold permanganate solution only with great difficulty, but at the water-bath temperature it is oxidised in alkaline solution, yielding caronic acid, the presence of the dimethylcyclopropane nucleus thus being confirmed. With acid permanganate, another acid, apparently isomeric with caronic acid, but not yet described, is produced.

By the action of alkalis, however, the substance loses the elements of hydrogen cyanide, and if hot dilute aqueous alkali is used in presence of ferrous hydroxide to facilitate this reaction, the volatile product being allowed to pass away at once in the steam, eucarvone is obtained. The product which cyanocarone should normally yield by the action of alkali is the $\alpha\beta$ -unsaturated ketone:

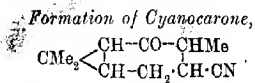


or the hypothetical intermediate product in the preparation of eucarvone from carvone hydrobromide. It follows, therefore, that at 100°, even in presence of quite dilute aqueous alkali, this substance is unstable, and is at once converted into eucarvone. As the cyanocarone certainly contains the *cyclopropane* ring, which is not stable to alkali, it seems certain that the presence of the ethylenic linking in the six-carbon ring to which the *cyclopropane* nucleus is attached does in fact render the molecule unstable, and leads mainly to the opening of the three-carbon ring at the point indicated by the dotted line.

The matter is of further general interest, too, in contrasting the modes in which the *cyclopropane* nucleus breaks down under varying conditions. It would not appear reasonable to suggest that the complex $\cdot\text{CMe}_2\cdot\text{CH}\cdot$ is less stable than $\cdot\text{CH}\cdot\text{CH}\cdot$, as under the influence of halogen hydride it is the former which is resolved. Nor can it be maintained that either is in such a position with reference to the keto- or cyano-group as would render it more liable to attack on this account. It would rather appear that when the carbon ring is saturated there is the less strain when the ring is composed of six atoms, but when there is an ethylenic linking in the nucleus at least in certain positions, then the reverse obtains, and the smaller ring is the less stable one.

EXPERIMENTAL.

Formation of Cyanocarone,



The hydrobromide of cyanodihydrocarvone, prepared as described by Lapworth (Trans., 1906, 89, 1826), was rapidly crystallised from alcohol, and treated in the following manner. The hydrobromide (160 grams) was suspended in methyl alcohol (300 c.c.), cooled to 0°, and to the pasty mixture an ice-cold solution of potassium hydroxide (36 grams) in methyl alcohol (150 c.c.) was added gradually with frequent agitation. The resulting liquid

was kept for some hours, while it gradually assumed a violet colour, potassium bromide being deposited. The whole was then saturated with carbon dioxide, and the precipitated potassium bromide and bicarbonate separated by filtration; the methyl alcohol was removed by distillation, and the volatile material expelled with the aid of a rapid current of steam. In some experiments the oil remaining in the distillation flask solidified on cooling, but it was found to be advantageous, as a rule, to shake the semi-solid material for some time with an ice-cold solution of potassium permanganate, added gradually until the colour of the latter was no longer discharged, the excess of permanganate and the precipitated manganese dioxide being subsequently removed by sulphur dioxide. The crude cyanocarone, which solidified on again cooling the liquid, was collected, and crystallised several times from alcohol:

0.2158 gave 0.589 CO_2 and 0.166 H_2O . $\text{C}=74.4$; $\text{H}=8.55$.

0.2206 „ 0.606 CO_2 „ 0.172 H_2O . $\text{C}=74.9$; $\text{H}=8.66$.

0.1264 „ 9.0 c.c. N_2 (moist) at 19° and 757 mm.; $\text{N}=8.15$.

$\text{C}_{11}\text{H}_{15}\text{ON}$ requires $\text{C}=74.6$; $\text{H}=8.47$; $\text{N}=7.92$ per cent.

Cyanocarone is very soluble in ethyl and methyl alcohols, ether, acetone, benzene, or ethyl bromide, fairly so in light petroleum, and almost insoluble in water. It crystallises with great readiness from its alcoholic solution in large, colourless, six-sided, transparent crystals, which melt sharply at $54-55^\circ$. When strongly heated, cyanocarone boils and distils with some decomposition above 300° .

0.201, made up to 25.05 c.c. with absolute alcohol, at 18° gave, in a 2-dcm. tube, $\alpha_D + 4.79^\circ$, whence $[\alpha]_D + 298^\circ$.

0.2306, made up to 25.1 c.c. with absolute alcohol, at 20° gave, in a 2-dcm. tube, $\alpha_D + 5.45^\circ$, whence $[\alpha]_D + 297^\circ$.

Cyanocarone is only very slowly attacked by a cold aqueous solution of potassium permanganate, or by a solution of the same salt in acetone at the boiling point of the solvent. It does not decolorise a solution of bromine in glacial acetic acid in presence of sodium acetate.

The *semicarbazide*, $\text{C}_{11}\text{H}_{15}\text{N}_3\text{N}_2\text{H}\cdot\text{CO}\cdot\text{NH}_2$, crystallises from alcohol in thin, flat, rectangular plates, which melt rather indefinitely, and decompose slightly at $218-221^\circ$:

0.1523 gave 31.6 c.c. N_2 (moist) at 15° and 758 mm. $\text{N}=24.18$.

$\text{C}_{12}\text{H}_{18}\text{ON}_4$ requires $\text{N}=23.93$ per cent.

Cyanocarone also yields an oxime, but this could not be obtained in crystalline form.

Action of Alkali and Ferrous Hydroxide on Cyanocarone.

On boiling cyanocarone with a 10 per cent. sodium hydroxide solution, an oil with a peppermint-like odour is produced, and the aqueous solution gives the reactions of a cyanide. The removal of hydrogen cyanide appears to take place more readily in presence of ferrous hydroxide, and for the investigation of this decomposition the following conditions were employed. Twenty grams of cyanocarone, 12 grams of potassium hydroxide, 4 grams of ferrous chloride, and 150 c.c. of water were gently heated in a flask attached to a condenser, and the water which distilled over, carrying with it the odorous oil, was replaced by gradually adding water to the flask. The process was continued until the aqueous distillate no longer contained an appreciable quantity of oil. The distillate was then saturated with common salt, and the oil extracted with ether. On fractionation, 4.4 grams of liquid boiling between 205° and 208°, and 1.1 grams boiling between 208° and 215° were obtained, a small amount of residue, which underwent decomposition on further heating, remaining in the distilling flask.

The oil thus obtained readily decolorised a solution of bromine, and gave a reddish-violet colour on boiling with methyl-alcoholic potash. It yielded an easily crystallisable semicarbazide, which, on recrystallisation from alcohol, melted at 183—184°:

0.1978 gave 35.5 c.c. N_2 (moist) at 19° and 751 mm. $N = 20.38$.

$C_{11}H_{17}ON_3$ requires $N = 20.29$ per cent.

On mixing this semicarbazide with eucarvone semicarbazide, prepared as described by Wallach and Löhr (*Annalen*, 1899, **305**, 237), the mixture melted at 183—184°; the product, after repeated crystallisation from methyl and ethyl alcohols, was optically inactive. The conversion of cyanocarone into eucarvone by the above process is not quantitative, and a considerable amount of a white substance crystallises out of the aqueous residue. This was isolated by diluting the residual liquid in the flask with water, heating to boiling, and filtering, when, on cooling, the substance separated, and was purified by recrystallisation from water, and finally from alcohol:

0.2278 gave 0.5630 CO_2 and 0.1786 H_2O . $C = 67.43$; $H = 8.72$.

0.203 „ 13.3 c.c. N_2 (moist) at 20° and 756 mm. $N = 7.45$.

$C_{11}H_{17}O_2N$ requires $C = 67.69$; $H = 8.72$; $N = 7.18$ per cent.

The substance has the properties of a saturated lactam or anhydramide, it is unaffected by a cold potassium permanganate solution, or by boiling aqueous or alcoholic potassium hydroxide

solutions, and is only slowly changed by fusion with potassium hydroxide and a few drops of water. It crystallises from water or alcohol in square plates or cubes, melting at 210–212°.

Action of Hydrogen Halides on Cyanocarone.

When heated with concentrated hydrochloric acid on the water-bath, cyanocarone yielded an acidic substance, which appeared to be a mixture of the stereoisomeric dihydrocarvonecarboxylic acids (Trans., 1906, 89, 1823); from this after repeated crystallisation from carbon tetrachloride and finally ethyl acetate, an unsaturated acid melting at 141–142° was obtained, which was identified by the mixed melting-point method as β -dihydrocarvonecarboxylic acid. With a cold saturated solution of hydrogen chloride, cyanocarone is first converted into a hydrogen chloride additive product identical with that obtained from cyanodihydrocarvone, the cyclopropane ring undergoing fission. This substance on further treatment with hydrochloric acid loses the elements of hydrogen chloride, and the $\cdot\text{CN}$ group is converted into the $\text{CO}\cdot\text{NH}_2$ group, the amide of the unsaturated dihydrocarvonecarboxylic acid being formed. Twenty grams of cyanocarone were suspended in 100 c.c. of concentrated hydrochloric acid, and the mixture was saturated with hydrogen chloride in the cold. The cyanocarone dissolved, and after a short time a white, crystalline substance separated, which was purified by crystallisation from alcohol:

0.3035, after being heated with fuming nitric acid and 0.325 of silver nitrate, required 4.5 c.c. of 0.112*N*-thiocyanate.
Cl=16.5.

$\text{C}_{11}\text{H}_{16}\text{ONCl}$ requires Cl=16.6 per cent.

The substance crystallised from alcohol in flattened, prismatic needles, melting at 69°, and when mixed with cyanodihydrocarvone hydrochloride its melting point was unaltered.

0.402, made up to 25 c.c. with absolute alcohol, at 18°, gave, in a 2-dem. tube, $\alpha_D + 0.82^\circ$, whence $[\alpha]_D + 25.6^\circ$. Cyanodihydrocarvone hydrochloride has $[\alpha]_D + 25.3^\circ$ at 18° (Trans., 1906, 89, 1826).

When cyanocarone is dissolved in a saturated solution of hydrogen bromide in glacial acetic acid, and kept for some time, a crystalline substance separates, of which a further amount can be obtained by diluting the acetic acid solution with water; this was collected and crystallised from alcohol:

0.2964, after being heated with fuming nitric acid and 0.2478 of silver nitrate, required 2.68 c.c. of 0.112*N*-thiocyanate.
Br=30.7.

$\text{C}_{11}\text{H}_{16}\text{ONBr}$ requires Br=31.0 per cent.

The substance crystallised from alcohol in flattened needles, melting at 85° , and on mixing it with cyanodihydrocarvone hydrobromide, its melting point was unaltered:

0.3546, made up to 25.1 c.c. with absolute alcohol, at 14° , gave, in a 2-dcm. tube, $n_D + 0.72^{\circ}$, whence $[\alpha]_D + 25.5^{\circ}$.

0.3208 of cyanodihydrocarvone hydrobromide, made up to 24.9 c.c. with absolute alcohol, at 14° , gave, in a 2-dcm. tube, $n_D + 0.665^{\circ}$, whence $[\alpha]_D + 25.8^{\circ}$.

Unsaturated Amide.—When cyanocarone is allowed to remain with saturated aqueous hydrogen chloride for some hours, the hydrochloride at first formed slowly dissolves. When the liquid no longer gave the reactions of a nitrile, it was diluted with twice its volume of water, and rendered alkaline with strong ammonia. After cooling, the separated solid was collected and crystallised several times from water:

0.2055 gave 0.5120 CO_2 and 0.1648 H_2O . $\text{C} = 68.0$; $\text{H} = 8.91$.

0.2022 „ 12.8 c.c. N_2 (moist) at 18° and 751 mm. $\text{N} = 7.22$.

$\text{C}_{11}\text{H}_{17}\text{O}_2\text{N}_2$ requires $\text{C} = 67.7$; $\text{H} = 8.72$; $\text{N} = 7.18$ per cent.

0.2335, made up to 25 c.c. with absolute alcohol, at 18.5° , gave, in a 2-dcm. tube, $n_D + 1.33^{\circ}$, whence $[\alpha]_D + 71.2^{\circ}$.

The amide is readily soluble in hot water or benzene, very soluble in alcohol, acetone, chloroform, or ethyl acetate, and sparingly so in cold water or light petroleum. It crystallises from alcohol or water in small, flattened, white needles, melting at 130° .

It evolves ammonia when boiled with 10 per cent. aqueous sodium hydroxide, reduces permanganate solution immediately in the cold, and decolorises a solution of bromine in acetic acid in presence of sodium acetate.

When heated on the water-bath with concentrated hydrochloric acid, the amide was converted into an acidic substance, which, on dilution, was precipitated as an oil; this was collected, and finally obtained as a solid, which was recrystallised several times from ethyl acetate. It melted at 141 – 142° , and when mixed with β -dihydrocarvonecarboxylic acid its melting point was unaltered. The amide was therefore in all probability an isomeride of the dihydrocarvonecarboxylic amide previously described (Trans., 1906, 89, 958).

Oxidation of Cyanocarone.

An aqueous solution of potassium permanganate oxidises cyanocarone fairly rapidly when heated with it on the water-bath. A solution of 140 grams of potassium permanganate in 3500 c.c. of water was added gradually to a mixture of 20 grams of cyanocarone and 200 c.c. of water. The liquid was filtered from the

precipitated manganese dioxide, evaporated to small bulk, saturated with salt, and extracted with ether twice to remove any unchanged cyanocarone or other neutral material. The liquid was then acidified with hydrochloric acid, and extracted twelve times with ether. The extracted material was freed from volatile material in the usual manner, and was finally obtained as a dark semi-solid mass. This was purified by triturating it with chloroform, and crystallising from a relatively small quantity of chloroform, using a Soxhlet extractor, as it is sparingly soluble in this solvent. After a subsequent crystallisation from water, it was dried at 100° :

0.2065 gave 0.4012 CO_2 and 0.1168 H_2O . $\text{C}=52.98$; $\text{H}=6.28$.

$\text{C}_7\text{H}_{10}\text{O}_4$ requires $\text{C}=53.16$; $\text{H}=6.33$ per cent.

0.1075 required 13.5 c.c. of $N/10$ -sodium hydroxide at -5° for neutralisation, using phenolphthalein as indicator, whence the equivalent=79.6. A dibasic acid, $\text{C}_7\text{H}_{10}\text{O}_4$, requires equivalent=79.

The acid crystallised from water in small, white masses, melting at $173-174^{\circ}$. The anhydride, prepared from the acid by means of acetyl chloride, was crystallised from light petroleum, and was found to melt at 55° .

The properties of the acid prove it to be identical with the *cis*-caronic acid prepared by Baeyer and Ipatieff from carone (*Ber.*, 1896, 29, 2796), and synthesised by Perkin and Thorpe (*Trans.*, 1899, 75, 48).

The first experiment on the oxidation of cyanocarone was carried out with an aqueous solution of potassium permanganate containing rather more sulphuric acid than that required to combine with the potassium hydroxide which is formed during the oxidation. In this instance, an acid similar in solubility to caronic acid was isolated, which melted, however, at 204° . On titration with sodium hydroxide solution, 0.104 required 6.15 c.c. of 0.1075 N -alkali for neutralisation, using phenolphthalein as indicator, whence equivalent=157.3. On adding a further 7 c.c. of the alkali and heating for one hour on the water-bath, the excess of alkali required 0.9 c.c. of 0.1003 N -hydrochloric acid for neutralisation, whence the equivalent calculated from the total amount of alkali neutralised=79.

The data indicate that the substance is the lactone of a saturated hydroxydicarboxylic acid, and probably isomeric with terebic acid.

III.—*The Influence of Water on the Availability of Hydrogen Chloride in Alcoholic Solution.*

By ARTHUR LAPWORTH and JAMES RIDDICK PARTINGTON.

IN recent communications by one of the authors, in part with E. Fitzgerald (Trans., 1908, 93, 2167 *et seq.*), evidence was adduced that during the esterification of a carboxylic acid or the hydrolysis of an ester, as brought about by the catalytic influence of hydrogen chloride, the velocity of reaction was nearly proportional to the concentration of the alcohol and the water respectively, although superficially the velocity of hydrolysis in alcohol or acetone, with a definite concentration of catalyst, appeared to be nearly independent of the concentration of the water over a wide range. The latter effect was attributed to a change in the availability of the catalyst, and was shown to be connected with the observations of Goldschmidt on the retarding influence of water on the esterification of carboxylic acids in alcoholic solution under the influence of mineral acids. Some preliminary experiments were also described which indicated that the phenomena were, as suggested, due in the main to changes in the salt-forming power or availability of the acid acting as catalytic agent, and on measuring the availability of the acid by the use of a weakly basic indicator, it was found that this was greatly altered by small changes in the water-content to an extent which corresponded, in order of magnitude at least, with the simultaneous changes in the velocity of esterification.

Pursuing this train of reasoning, it was demonstrated that the changes in the availability of the acid due to the introduction of water into its solution in alcohol, for example, could not be explained by aid of the view of salt-hydrolysis proposed by Arrhenius, hence, as the power which an acid has of forming complex ions with a weak base of the ammonia type must be proportional to the concentration of free hydrogen ions, other things being equal, it may be inferred that the water acts by diminishing the concentration of the free hydrogen ions if such are present. Consequently water appears to act by uniting with hydrogen ions, as does ammonia, to form complex hydriums. Also, since alcohol and water appear to play similar parts, combination of hydrogen ions with alcohol is probable. With respect to the conception that hydrogen ions unite with water or alcohol, no novelty was claimed, the possibility, even the probability, having been realised by many chemists since the date when the ionic-dissociation hypothesis was first proposed, and especially since the recent development of the oxonium theory.

Goldschmidt and Udby (*Zeitsch. physikal. Chem.*, 1907, 60, 728) had previously used the conception in discussing the kinetics of accelerated esterification, although theirs was an *ad hoc* application of the hypothesis, no attempt having been made by these authors to associate experimentally the anti-catalytic effect of water in esterification processes with alterations in the availability, or salt-forming power, of the acid, and even in applying the conception to the case of a very weak base present in small quantity in an alcoholic solution of hydrogen chloride (*loc. cit.*, p. 731) they picture the hydrated hydrions produced on addition of water as being formed exclusively at the expense of the small amount of salt derived from the weak base (carboxylic acid), which is very far from being the case, as all the salts of weak bases present and the free hydrogen ions, if there, would be diminished in the same proportion.

It is very important to realise that two quite distinct propositions are here involved. The first of these is, that the change in the catalytic activity of a mineral acid in organic solvents, on addition of water, is due to a change in the availability of the mineral acid, and is capable of experimental proof in the manner previously indicated by one of the present authors. The second one concerns the explanation which is to be given of this change in the availability of the mineral acid, and is at present almost wholly hypothetical in character. Fitzgerald and Lapworth, who approached the question from this point of view, were the first to advance the former as a definite proposition, and to indicate the manner in which it might be experimentally established. Goldschmidt and Udby, on the other hand, had previously employed the hypothesis of combination of hydrogen ions with alcohol and water respectively, in explanation of the anti-catalytic effect of water on esterification in alcoholic solution; but as they did not fully realise that the determining factor was the change in the availability of the mineral acid (which naturally depends almost wholly on the alcohol and the water, and only to an almost inappreciable extent on the small quantity of feebly basic carboxylic acid), they applied the hypothesis in an incorrect manner to the calculation of ξ , the concentration of complex hydrions formed by the carboxylic acid (*loc. cit.*, p. 731), entirely overlooking the necessity of taking into consideration the influence of the alcohol used as solvent.

A suggestion made by Goldschmidt and Udby, previously misunderstood by Lapworth, is of great importance in its bearing on the hypothesis of hydrogen ion hydration, and attention may again be drawn to it here. These authors attribute the abnormally large increase in the esterification velocity constant with increasing concentration of catalyst observed in alcohol containing water to the

removal of part of the free water by combination with part of the catalyst (*loc. cit.*, p. 733—735 and 751 *et seq.*; compare also *Proc.*, 1909, 25, 19; *Trans.*, 1908, 93, 2196 and 2197, where the mass of the free water was assumed nearly constant). This explanation (although, in the generalised form given by these authors, it disregards the well-known stimulating effect of anions on the catalytic action of strong acids) is probably correct so far as it applies to the abnormal case where the concentration of the catalyst and the water are comparable, and further investigation of this particular point would appear to be one of the most promising modes of adducing direct evidence as to the correctness or otherwise of the hypothesis of chemical combination between hydrogen ions and solvent.

The present paper contains an account of work done in the expectation of finding that the determining factor in the influence of water on catalysis by mineral acids in alcoholic solution is the availability of the acid for salt formation. The "availability" of an acid may be defined as a function proportional to its capacity for forming complex hydrions with any mon-acid base, and at any moment the concentration of these complex ions is given by $\xi = k.BP$, where k is a constant for the base in the medium used, B the concentration of the free base, and P the "availability" of the acid, or $P = \frac{\xi}{k.B}$. At present it is only feasible to determine the relative values of k for different bases, hence P here has also only a relative magnitude.*

In order to avoid for the present all hypothesis as to the state of a mineral acid in alcoholic solution, an expression for the change in the availability of a mineral acid in absolute alcohol may be developed on the facts adduced by Goldschmidt and by Goldschmidt and Udby.

These authors found that the velocity of esterification in absolute alcoholic solution was proportional to the number of "hydrogen ions," or with a monobasic mineral acid as catalyst, to the product of its concentration and the degree of dissociation. This, however, is also proportional to the concentration of complex hydrions which the acid would yield with a definite concentration of a free mon-acid base, or, in other words, their work affords the proof that in absolute alcohol the velocity of esterification is *ceteris paribus* proportional to the availability of the acid as above defined.

Now Goldschmidt and Udby also find that with a given concentration of mineral acid and carboxylic acid, the velocity of esterification is

* The availability here corresponds with the function $R/V\Sigma M\phi$ developed in a previous paper (*loc. cit.*, p. 2195), where R is the degree of dissociation of the acid; V = the volume which contains one gram-equivalent of acid, M and ϕ corresponding with B and k respectively.

nearly proportional to $\frac{1}{r+w}$, where r is a constant which depends only on the alcohol, and w is the concentration of the water. The contribution which Fitzgerald and Lapworth claim to have made here, is in pointing out that the form of the esterification curve in alcohol departs from the unimolecular type only to the extent that the condition of the catalyst alters, $\frac{1}{r+w}$ being merely a measure of the availability of the catalyst; in other words, the velocity of esterification is proportional to the availability of the catalyst, not only in absolute alcohol, but in moist alcohol too, and $P = \frac{P_0 r}{r+w}$, where P_0 is the availability when $w=0$. It may be noted that with any given state of the mixture of alcohol and water the availability is also proportional to the concentration of the catalyst, hence

$$P = X \cdot c \cdot \frac{p \cdot r}{r+w},$$

where c = the concentration of the catalyst, p = its availability when $c=1$ and $w=0$, and X = the degree of dissociation as measured by the electrical conductivity method in a medium having that particular composition. For the highly dilute solutions discussed in the following paragraphs, X is assumed constant.

One of the present authors has already shown that this is the conclusion which must be derived if the hypothesis of combination of the hydrogen ions with the alcohol, the water, and the carboxylic acid be adopted (Trans., 1908, 93, 2195), as the availability must be proportional to the concentration of the free hydrogen ions if these are present.

In order to prove experimentally that this conclusion is the correct one, it is necessary to show that the salt-forming capacity of a very dilute mineral acid varies as $\frac{1}{r+w}$, where r is identical with that calculated from the results of esterification velocity determinations. For the purpose a very weakly basic indicator may be used, and the amount of salt formed with a given concentration of base estimated by colorimetric methods. In practice this is difficult to do, and a somewhat different mode of treatment must be employed, namely, to keep the amount of salt and base nearly constant by varying the concentration of the mineral acid and the water simultaneously. In this case the application of the law of mass action to the definition of availability gives $\xi = k \cdot B \cdot P$, which in terms of the authors' theory is $= k B \cdot \frac{p \cdot c \cdot r}{r+w}$, where ξ = the concentration of the complex hydrions,

When ξ and B are constant, then P is also constant, consequently $\frac{c}{r+w}$ is a constant, say K .

It is shown in the practical part of the paper that (1) in these circumstances $\frac{c}{r+w}$ is experimentally nearly constant for salt formation; and (2) with different indicators the value of r is identical with that obtained by observations on the velocity of esterification, within the limits of experimental error, which, it must be admitted, are at present considerable owing to the very small value of r , the measure of the basic affinity of absolute alcohol, and also because of the considerable influence of the merest traces of impurity on the availability of the highly dilute acid which it was necessary to use.

The accurate measurement of the availability of acids in organic media is at present very difficult, owing to circumstances which have already been discussed, and the means which is the most generally applicable, as yet, is that based on determinations of the velocity of esterification, since the basic affinity of alcohols and carboxylic acids is small and less likely to disturb the availability of the highly dilute acid than when indicators, amides, or other definitely basic compounds are introduced; moreover, a carboxylic acid may be chosen to suit a solution of any desired degree of acidity. At the time of the publication of his first paper, and that with E. Fitzgerald, one of us had in view the determination of the availability of acids in various media, simple and mixed, by the electrical method applied in the hydrogen electrode, which, apart from disturbing influences and boundary effects, should theoretically be capable of giving the ratio of the availabilities of an acid in solutions contained in two intercommunicating cells, entirely apart from the reality or otherwise of "free hydrogen ions." Acree has recently drawn attention to the possibility of using the principle of the hydrogen electrode in connexion with experiments on catalysis for the measurement of the concentration of free hydrogen ions (*Amer. Chem. J.*, 1909, **41**, 482). It would be most interesting to obtain confirmation by this means of the "availability formula," $P = \frac{k.c.}{r+w}$, for hydrogen chloride in strong alcohol.

The method should also be applicable to the determination of the relative strengths of bases, weaker than water, in alcoholic and other solutions. Such estimation might also be made by using esterification or tintometric processes, as was previously suggested (*Trans.*, 1908, **93**, 2199), but in connexion with the preliminary numbers previously given, it is necessary to state that the method of determination

employed necessarily leads to quite discrepant values for the affinities of very weak bases, owing to a number of sources of error which were not realised at that time. It was assumed, for example, that most of the base added was in the free state, which is by no means the case when a base such as carbamide competes with alcohol for the acid; moreover, the presence of traces of basic impurities in the material will affect the availability of even a relatively large quantity of an acid when this happens to be one which is feebly ionised, as is the case with trichloroacetic acid in benzene, and our experiments show clearly how difficult it is to be certain that basic impurities in important quantities are absent. With a fuller realisation of these and other points of difficulty it is proposed to undertake the study of affinity constants of some very weak bases in alcoholic solution, in the hope of devising trustworthy methods of measurement.

The hydrogen electrode may also prove useful in investigating the changes in the availability of acids in acetone and in ether. In these, which, as is well known, are poor ionising solvents for hydrogen chloride, acids behave in a remarkable manner towards the first traces of moisture. In pure dry acetone, the first small additions of water do not cause any marked fall in the availability of dissolved hydrogen chloride, although with larger amounts the availability falls off much as it does in alcohol, as is indicated by the numbers given by Fitzgerald and Lapworth for ester hydrolysis and for esterification in moist acetone. In dry ether, again, a very small quantity of water actually causes a decided increase in the availability. These points were first noted during experiments which Mr. Fitzgerald has been conducting on the velocity of esterification in initially dry acetone and ether; here abnormalities were observed in the esterification curve with the former as solvent, while with the latter the curves showed a point of inflexion; tintometric experiments confirmed the conclusion that this was a phenomenon dependent on the availability of the catalyst, and were of interest as adding some weight to the contention that the much discussed changes in the velocity of esterification are due to static causes not connected with the mechanism of reaction except in so far as the availability of the catalyst is concerned.

Experiments on the application of the hydrogen electrode to these questions are now in progress.

EXPERIMENTAL.

The alcohol employed in these determinations was prepared from five distinct specimens, *A*, *B*, *C*, *D*, and *E*. *A* was made from a sample of 96 per cent. spirit by heating it with lime for three days, and subsequently treating the resulting nearly dry alcohol with excess of

calcium. Samples *B*, *C*, *D*, and *E* were made from three different specimens of commercial absolute alcohol. In all cases the last traces of moisture were removed by heating the alcohol with a considerable excess of calcium turnings until a sample of the liquid on addition of water set to a jelly-like mass, indicating that calcium ethoxide was present, and the dried liquid was then directly distilled, the vapour being passed through a trap containing glass wool, the first and last portions rejected, and the middle fraction collected in a dried flask provided with a soda-lime tube to ensure the absence of moisture. The test applied for the presence of calcium ethoxide afforded full proof that the dehydration was as complete as the process was capable of effecting, and further treatment with calcium was obviously superfluous; this conclusion was confirmed by the approximate constancy of the low water value of the four specimens of alcohol obtained in this manner.

Tintometric Experiments.

Aminoazobenzene is an extremely sensitive indicator to hydrogen chloride in absolute alcohol, and was only suitable for concentrations of acid between $N/10,000$ and $N/100,000$, so that errors due to traces of impurities were liable to be unreasonably large. Many other indicators were tried, but the only one having a very decided advantage over aminoazobenzene was an azo-derivative of diphenylamine, the sensitiveness of which was considerably less than that of aminoazobenzene. Further investigation may lead to the discovery of still less basic indicators, more useful than these, for investigations in such solvents as absolute alcohol with higher concentrations of mineral acid.

The principle of the method used throughout has already been discussed; the procedure was to run a definite volume of a solution of alcoholic hydrogen chloride into the absolute alcohol under investigation, partly to discharge the colour by addition of a minute quantity of water, and then to restore the original tint by adding more of the alcoholic hydrogen chloride.

The alcoholic hydrogen chloride and the water were measured from narrow, graduated tubes discharging the liquid from a capillary exit; these tubes had been carefully calibrated, and the errors in reading the small volumes of liquid and those due to alterations in bulk of the original alcohol under investigation were usually within the limits of the experimental error due to other causes. The discrepancies at first were very marked, often leading to differences of 25 per cent. in the "water value" for any specimen of absolute alcohol, and this was finally traced to the effect of the laboratory air with which the

solutions were unavoidably brought into contact during the operation of thoroughly mixing the added acid or water. When the solutions were stirred in the ordinary way with a bent glass rod, it was noticed, especially with the extremely dilute solution of hydrogen chloride employed and with aminoazobenzene as indicator, that very decided changes in the colour occurred in the tintometer, indicating a diminution in the acidity of the solutions. This was due mainly neither to carbon dioxide nor aqueous vapour, as pure dry carbon dioxide had no appreciable influence, and the laboratory air, after being passed through a tube of lime or soda-lime, still produced the same effect. If air dried over sulphuric acid was used to stir the solution, however, the tint did not change, so that the effect was doubtless due to traces of ammonia or some other powerfully basic impurity in the atmosphere. Further, the solutions, if undisturbed or stirred by twisting a spiral glass rod in the solution, did not alter in tint appreciably during the time occupied in an experiment, so that the latter method was finally adopted when using the tubes of a colorimeter to contain the specimens of alcohol.

In all cases 50 c.c. of the specimen of absolute alcohol were used, but three distinct modes of measurement were employed, the temperature of the alcohol in all cases being within two degrees of 25°, except when it is stated otherwise.

(1) The alcohol containing the indicator was contained in a 50 c.c. flask, and alcoholic hydrogen chloride having the same concentration of indicator as the original alcohol was added until the tint was as nearly as possible identical with that in a standard specimen in a similar flask; water was then introduced, and more alcoholic hydrogen chloride to restore as nearly as possible the original tint, this process being repeated several times, the added volume noted in each case, and the water value of the alcohol determined by a graphic method or by the method of least squares.

(2) The alcohol with a trace of indicator was contained in one of the tubes of a colorimeter and tinted by alcoholic hydrogen chloride to nearly the same colour as that of the liquid in the standard tube of the instrument, the exact depth of the standard liquid required to produce a balance being noted. After addition of a measured volume of water, more hydrogen chloride solution was added, and the tint balanced by varying the depth of the standard solution. More hydrogen chloride was then added, the tint again balanced, and so on until a reasonably large number of readings had been made; in this case the depth of the standard solution was found experimentally to be proportional to the hydrogen chloride present when the amount of water was constant, so that the corrections were easily applied.

(3) As in (2), but much more indicator was employed, and the tint

was viewed through a deep blue screen. The depth of the standard liquid was not proportional to the amount of hydrogen chloride in the alcohol, so that separate experiments had to be made to determine the correction formula.

In cases (2) and (3) the water values were at first estimated by a modification of the method of least squares, but this was afterwards abandoned, as they could be obtained graphically within the limits of experimental error.

It will be unnecessary to go into detail in each case, but one or two typical instances of each kind may be given, with the object of indicating the mode of calculation, as well as to show that the formula $P = \frac{kc}{r+w}$ applies here.

TYPE I.

Indicator: Aminoazobenzene. Hydrochloric acid = $N/100$ nearly.

W = water present in c.c.

H = volume of alcoholic hydrogen chloride added in c.c.

A = total volume of alcohol.

$h = \frac{H}{A} A_0$, or quantity of acid per 50 c.c. of alcohol.

R = the water value, in grams, of 50 c.c. of the alcohol used.

$W' = \frac{50W}{A}$, or the amount of water per 50 c.c. of alcohol.

$$C = \frac{h}{W' + R}.$$

W .	H .	A .	h .	W' .	C .
0.00	1.00	51.0	1.00	0.000	10.3
0.09	2.00	52.0	1.96	0.086	10.7
0.18	2.83	52.8	2.73	0.171	10.2
0.36	4.70	54.7	4.31	0.329	10.1
0.72	8.40	58.4	7.34	0.616	10.3

R = water value per 50 c.c. of the alcohol at $25^\circ = 0.097$ gram, whence $r = 10.8$.

For the applicability of the formula $P = \frac{kc}{r+w}$ (see above), the value of C should be constant.

TYPE III.

Indicator: *p*-Tolueneazodiphenylamine, used with blue screen. Strength of alcoholic hydrogen chloride added was between $N/5$ and $N/10$. (In these cases no correction was needed for the relatively small volume of alcoholic hydrogen chloride added, which did not amount to more than 2 per cent. of the total volume of alcohol used.)

W = c.c. of water present (in 50 c.c. of alcohol).

H = volume of alcoholic hydrogen chloride in c.c.

l = height of adjustable column of standard liquid in cm.

A series of measurements showed that under the conditions and within the limits used, the product $H \times \left(\frac{1}{l} - 0.04\right)$ was constant with absolute alcohol, or with alcohol containing any fixed concentration of water. Hence this product was equal to $H_o \times \left(\frac{1}{l_o} - 0.04\right)$, where H_o is the volume of alcoholic hydrogen chloride, which would be necessary to produce any standard tint corresponding with the fixed height, l_o .

As $\left(\frac{1}{l_o} - 0.04\right)$ is constant, then for any two observations the relation between the amounts of acid H_o and H_o' required to produce

a standard tint was given by $\frac{H_o}{H_o'} = \frac{H \times \left(\frac{1}{l} - 0.04\right)}{H' \times \left(\frac{1}{l'} - 0.04\right)}$; or the product

$H \times \left(\frac{1}{l} - 0.04\right)$ is proportional to the amount of hydrogen chloride required to produce any definite standard tint with a fixed water-content.

Two instances are given. The first to indicate the applicability of the foregoing correction formula, and the second to demonstrate that the formula $H_o = (r + w) \times \text{a constant}$ is applicable when the water varies in amount, and, therefore, $P = \frac{k}{r + w}$ when the amount of hydrogen chloride is constant (compare p. 23).

EXAMPLE I.

W .	l .	B .	H .	$H \times B$.	C .
0.0	7.85	0.0876	0.25	0.0219	2.38
0.0	8.40	0.0790	0.28	0.0221	2.40
0.0	8.95	0.0717	0.30	0.0215	2.33
0.074	8.35	0.0798	0.50	0.0399	2.40
0.074	8.70	0.0749	0.53	0.0397	2.39
0.074	8.95	0.0717	0.55	0.0394	2.37
0.221	8.10	0.0835	0.90	0.07615	2.40
0.221	8.55	0.0770	0.97	0.0748	2.39
0.221	8.65	0.0730	1.04	0.0759	2.42

The water value, R , of 50 c.c. of the alcohol used was = 0.092 gram. The column headed B contains the values of $\left(\frac{1}{l} - 0.04\right)$, and C , those of $\frac{H \times B}{R + W}$.

The applicability of the correction formula $H \times \left(\frac{1}{l} - 0.04\right)$ is shown by the close agreement between the bracketed values of $H \times B$.

The applicability of the availability formula $P = k \frac{C}{r + w}$ is shown by the approximate constancy in the values of C throughout.

EXAMPLE II.

W .	L .	B .	H .	$H \times B$.	C .
0.0	48.40	0.0790	0.165	0.01304	1.37
0.0	8.79	0.0738	0.18	0.0133	1.40
0.0	8.62	0.0641	0.20	0.01282	1.35
0.0552	8.73	0.0746	0.29	0.0216	1.44
0.0552	9.03	0.0707	0.30	0.0212	1.41
0.1935	7.89	0.0867	0.46	0.0399	1.38
0.2655	7.55	0.0925	0.53	0.0490	1.36
0.3519	7.62	0.0912	0.68	0.0620	1.39
0.4329	7.87	0.0871	0.85	0.0740	1.40
0.486	8.47	0.0781	1.01	0.0789	1.36

R , or water value, = 0.095 gram for 50 c.c. of the absolute alcohol, whence $r = 0.106$ (or 1 litre of the absolute alcohol used was equivalent to 0.106 gram-molecules of water at 25°).

Esterification Experiments.

For the determination of the water value of the alcohol by the esterification process, purified phenylacetic acid dried in a vacuum over sulphuric acid was employed in all cases. The flasks employed were subjected to the action of a current of steam for a quarter of an hour, and then carefully dried before each experiment. The dry acid was only roughly measured, but the water in each case was weighed. From each sample of alcohol a solution of hydrogen chloride of about $N/10$ strength was prepared by passing the dried gas into a portion of the specimen, care being taken to exclude moisture. The alcoholic solutions before admixture were all first heated to the temperature of the thermostat, and the moment when the reaction commenced was noted. One or two titrations were always made near the commencement of the reaction for the purpose of obtaining the true initial titre by extrapolation, as this value was required for a knowledge of the exact amount of water present at any stage. The titre of the hydrogen chloride present at the beginning and end of each experiment was taken, using $N/100$ -silver nitrate, thus definitely ensuring constancy in the amount of catalyst.

Two flasks were always examined simultaneously, one containing the initially dry alcohol, and the other, alcohol containing initially a weighed quantity of water.

The intermediate values of the constants being the most trustworthy, the approximate water value of the alcohol is best gauged by comparing the intermediate values of the constants obtained for the two flasks. That is to say, the value of r was not ascertained by the reference to

the constancy of the value for any one experiment, but by comparing the numbers obtained in the two experiments.

This method commends itself as the best, since the more trustworthy values for the velocity are of course those calculated from the time when the change has become steady to a point not far from half way towards the end. All the titres, y , are corrected for the hydrochloric acid present.

The bracketed values of the titre y for $T = 0$ were obtained by graphic extrapolation from the first few observations, for which no constant was calculated. R was calculated throughout from the formula corresponding with that used by Goldschmidt and Udby as

$$-\frac{dy}{dt} = kc \cdot \frac{y}{R + W + y_0 - y}$$

when the concentration of the catalyst is constant,

$$\text{whence } kc = \frac{(R + W + y_0)(\log_e y_1 - \log_e y) - (y_1 - y)}{T - T_1},$$

where R = the water equivalent of 10 c.c. of the alcohol used in $N/10$ c.c.

W = the equivalent of the initially added water.

y = the titre of 10 c.c. of the solution at the time T .

y_0 = initial titre [bracketed value] of 10 c.c. of the solution calculated by extrapolation.

y_1 = the first titre actually made at the time T_1 .

The time is given in minutes, and the titres are c.c. of $N/10$ -alkali required to neutralise the free phenylacetic acid present in 10 c.c. of the solution investigated.

(r in all cases in this paper refers to the water equivalent in gram-molecules of one litre of alcohol.)

Esterification Results for Specimen A.

Each flask had a capacity of 100 c.c. Amount of solution used for each titre = 10 c.c. Time in minutes. Titre given in c.c. of $N/10$ -sodium hydroxide. Hydrochloric acid during reaction was 0.0195 N , nearly.

Flask I.—No water.

T .	y .	kc , assuming			
		$r=0.15$.	$r=0.11$.	$r=0.10$.	$r=0.09$.
[0	9.93]	—	—	—	—
7	9.50	—	—	—	—
29	8.32	—	—	—	—
42	7.63	—	—	—	—
68	6.47	10.74	8.23	7.61	6.95
137	4.44	10.68	8.36	7.77	7.17
212	3.09	10.51	8.31	7.80	7.24
287	2.18	10.49	8.38	7.89	7.34
Mean.....		10.61	8.32	7.77	7.18

Flask II.—Water = 0.36 gram.

T.	y.	<i>k_c</i> , assuming			
		<i>r</i> = 0.15.	<i>r</i> = 0.11.	<i>r</i> = 0.10.	<i>r</i> = 0.09.
[0]	20.2]	—	—	—	—
15	19.50	—	—	—	—
30	18.81	—	—	—	—
69	17.10	8.96	7.87	7.76	7.50
138	14.62	9.16	8.21	7.96	7.70
216	12.30	9.08	8.11	7.91	7.68
446	7.91	8.86	8.04	7.82	7.59
Mean.....		9.02	8.06	7.87	7.62

The value of *r* evidently lies between 0.10 and 0.11.

A series of tintometric experiments for this specimen of absolute alcohol gave *r* = (i) 0.105, 0.101, 0.105.

(ii) 0.093, 0.101.

(iii) 0.105, 0.101, 0.101, 0.095.

Series B.—Each flask had a capacity of 50 c.c. Amount of solution used for each titration = 10 c.c. Time in minutes. Titre given in c.c. *N*/10-sodium hydroxide. Hydrochloric acid during reaction was 0.0140*N*, nearly.

Flask I.—With no water.

T.	y.	<i>k_c</i> , assuming			
		<i>r</i> = 0.15.	<i>r</i> = 0.11.	<i>r</i> = 0.10.	<i>r</i> = 0.09.
[0]	11.43]	—	—	—	—
12	10.80	—	—	—	—
98	7.52	7.32	5.63	5.21	4.77
220	5.02	6.95	5.48	5.11	4.73
303	3.75	7.17	5.73	5.36	5.00
Mean.....		7.15	5.61	5.23	4.83

Flask II.—With 0.18 gram of water.

T.	y.	<i>k_c</i> , assuming			
		<i>r</i> = 0.15.	<i>r</i> = 0.11.	<i>r</i> = 0.10.	<i>r</i> = 0.09.
[0]	10.50]	—	—	—	—
10	10.30	—	—	—	—
95	8.88	6.28	5.57	5.40	5.23
205	7.30	6.49	5.77	5.61	5.43
300	6.26	6.41	5.74	5.56	5.39
Mean.....		6.39	5.69	5.52	5.35

The value of *r* evidently lies just above 0.11.

Tintometric measurements gave *r* = { (ii) 0.098, 0.106, 0.108.
(iii) 0.108, 0.098, 0.100.

Series C.—Each flask had a capacity of 50 c.c. Amount of solution used for titration = 10 c.c. Time in minutes. Titre given in c.c. of

32 LAPWORTH AND PARTINGTON: INFLUENCE OF WATER ON

N/10-sodium hydroxide. Hydrochloric acid during reaction was 0.0182*N*.

Flask I.—No water.

<i>T</i> .	<i>y</i> .	<i>kc</i> , assuming			
		<i>r</i> =0.15.	<i>r</i> =0.11.	<i>r</i> =0.10.	<i>r</i> =0.09.
[0	9.89]	—	—	—	—
11	8.83	—	8.22	7.58	6.83
27	7.93	10.81	7.98	7.42	6.84
96	5.86	10.34	7.90	7.36	6.83
186	3.48	10.00	—	—	—
Mean.....	—	10.38	8.03	7.44	6.85

Flask II.—Water = 0.1430 gram.

<i>T</i> .	<i>y</i> .	<i>kc</i> , assuming			
		<i>r</i> =0.15.	<i>r</i> =0.11.	<i>r</i> =0.10.	<i>r</i> =0.09.
[0	12.70]	—	—	—	—
22	11.73	—	7.93	7.64	7.33
67	10.35	9.04	7.79	7.54	7.28
260	6.43	8.80	7.77	7.50	7.27
437	3.85	8.76	—	—	—
Mean.....	—	8.87	7.83	7.56	7.31

From above, *r* is evidently between 0.10 and 0.11.

Tintometric experiments gave = *r* { (ii) 0.098, 0.095.
(iii) 0.101, 0.105.

Series *D*.—Each flask had a capacity of 100 c.c. Amount of solution titrated = 10 c.c. Time in minutes. Titres in terms of *N*/10-sodium hydroxide. Hydrochloric acid during reaction was 0.0278 *N*, nearly.

Flask I.—No water. Flask II.—Water = 0.10 gram.

Flask III.—Water = 0.20 gram.

<i>T</i> .	<i>y</i> .	<i>kc</i> (<i>r</i> =0.10).	<i>T</i> .	<i>y</i> .	<i>kc</i> (<i>r</i> =0.10).	<i>T</i> .	<i>y</i> .	<i>kc</i> (<i>r</i> =0.10).
[0	13.33]	—	[0	13.33]	—	[0	13.33]	—
14	12.05	—	18	12.30	—	21	12.47	—
42	9.71	—	44	10.89	—	46	11.08	—
66	8.19	0.987	71	9.16	0.986	73	8.91	0.987
126	5.95	1.008	131	6.83	0.992	131	7.73	1.001
221	3.48	0.985	225	4.50	1.001	227	5.43	1.007

Tintometric experiments gave *r* = 0.09 and 0.11 by (i).

Series *E*.—Each flask had a capacity of 100 c.c. Amount of solution titrated = 10 c.c. Time in minutes. Titres in terms of *N*/10-sodium hydroxide. Hydrochloric acid during reaction was 0.0201*N*, nearly.

AVAILABILITY OF HYDROGEN CHLORIDE

Flask I.—No water.

Flask II.—Water = 0.197 gram.

T.	kc ($r \approx 0.10$)	T.	y.	kc ($r = 0.10$)
0	—	0	12.7	—
11	—	20	11.75	—
25	—	50	10.45	—
116	0.865	129	8.18	0.787
120	0.809	230	5.15	0.815
272	0.792	249	4.05	0.805
372	0.788			
	Mean 0.798			Mean 0.802

whence $r = 0.10$.

Tinbergen's experiments gave $r =$ (ii) 0.090-0.099.
(iii) 0.095, 0.098, 0.090.

The apparent discrepancy between the values of r found, as above, and the value 0.15 found by Goldschmidt and Udby is apparently due mainly to the circumstance that they calculated the value for higher concentrations of catalyst. A comparison of the numbers for the velocity of reaction at low concentrations indicates that the alcohol used by these authors was probably as dry as that used in the experiment detailed in the present paper.

Summary

(i) The "availability" of a very dilute solution of hydrogen chloride in moist alcohol is nearly an inverse linear function of the amount of water present for quantities of water not exceeding a concentration of $N/2$.

(ii) The effect is a static one, and there is no reason to believe that the antagonistic effect of water is due to any other cause than a change in the availability of the acid; it is not, for instance, to any appreciable extent the result of any influences, such as increase in viscosity, tending to lower the measured velocity of reaction (on this point compare, however, S. E. Acree, *Amer. Chem. J.*, 1909, 41, 471), nor is it the result of ester hydrolysis.

(iii) The availability within the above range may be very nearly represented by $\frac{c}{c + 1}$, where c = concentration of the hydrogen chloride, 1 being a constant, w the concentration of water present, r being the water equivalent of the alcohol present.

(iv) r is a constant which depends on the alcohol (as Goldschmidt and Udby have demonstrated in the case of esterification), but, within the limits of experimental error, is the same whether the availability of the acid be measured by means of esterification velocities or by estimating the amount of the salt which the acid can form with a weak mon-acid base.

(v) For absolute alcohol dried over excess of calcium, r is about 0.10 for very low concentrations of hydrogen chloride at 25° ; thus, at this temperature, the availability of hydrochloric acid in absolute alcohol is lowered 50 per cent. by the addition of 1.8 grams of water per litre of alcohol.

(vi) If any free hydrogen ions exist in solutions of acids in water or alcohol, an assumption for which there is at present no direct evidence, then for small changes in the composition of the mixture of water and alcohol it may be concluded that the concentration of these is a measure of the availability of the acid.

(vii) The fundamental difference between the view of Goldschmidt and Uddy and that of Fitzgerald and Lapworth revolves on the point that the first-named workers, although realising that the catalyst is mostly shared between the alcohol and the water, neglected to consider the change in the availability of the catalyst when water is added to its alcoholic solution, and consequently they formed an incorrect conception of the manner in which water would affect the equilibrium between a dissolved weak base and its salt.

The authors desire to state that most of the cost of this investigation was defrayed by a grant from the Government Grant Research Fund of the Royal Society, and for this they wish to express their indebtedness.

SCHUNCK LABORATORY,
UNIVERSITY OF MANCHESTER.

IV.—Organic Derivatives of Antimony. Part I. *Tricamphorylstibine Chloride and Triphenylstibine Hydroxynitrate Hydroxysulfate.*

By GILBERT T. MORGAN, FRANCES M. G. MICKLETHWAIT, and
GEORGE STANFORD WHITBY, B.Sc., A.R.C.S.

A COMPARATIVE study of the interactions taking place between sodium camphor and the trichlorides of phosphorus, arsenic, and antimony has shown that in the case of the arsenic compound the principal products are dicamphorylarsinic and tricamphorylarsinic acids (Trans., 1908, 23, 2144; 1909, 95, 1473). The experiments with phosphorus trichloride are still in progress; the present communication deals with the case of antimony trichloride.

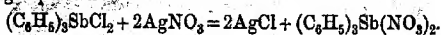
The interaction of sodium camphor and antimony trichloride in

dry toluene does not lead to the production of any substances soluble in aqueous alkali hydroxides or carbonates. The only product definitely isolated and identified is *tricamphorylstibine chloride*, $(C_{10}H_{15}O)_3SbCl_2$. This substance undergoes destructive hydrolysis so readily that the resulting tricamphorylstibine oxide, $(C_{10}H_{15}O)_3Sb_2O_3$, is always more or less contaminated with hydrated antimonious oxide arising from the decomposition of the chloride into hydrochloric and antimonious acids and camphor.

As one object of this research was to obtain an organic derivative of antimony sufficiently stable and soluble for employment as a therapeutic agent, attention was now directed to triphenylstibine chloride, $(C_6H_5)_3SbCl_2$, obtained by Michaelis and Reese by the interaction of chlorobenzene, antimony trichloride, and sodium (*Annalen*, 1886, 233, 43).

As these investigators have stated that this aromatic antimony derivative is possessed of considerable stability, attempts were made to convert this substance into compounds dissolving more readily in aqueous solutions.

When treated with alcoholic silver nitrate, triphenylstibine chloride loses its chlorine quantitatively in accordance with the following equation:



The triphenylstibine nitrate is not stable under these conditions, and undergoes partial hydrolysis into a definitely crystalline substance, *triphenylstibine hydroxynitrate*, $(C_6H_5)_3Sb(OH) \cdot NO_3$, which may be recrystallised from hot water without further hydrolysis. In connexion with the formation of this substance, it is of interest to note that Michaelis and Reese describe a triphenylstibine nitrate, prepared by dissolving triphenylstibine in hot fuming nitric acid (*loc. cit.*, p. 52), which is stated to be insoluble in water, but crystallisable from alcohol.

The substitution of silver sulphate for silver nitrate in the foregoing reaction leads to the production of the corresponding *triphenylstibine hydroxy sulphate*, $(C_6H_5)_3Sb(OH) \cdot SO_4 \cdot Sb(OH)(C_6H_5)_3$, which is less soluble in water than the hydroxynitrate.

EXPERIMENTAL.

Tricamphorylstibine Chloride.—On adding a toluene solution of antimony trichloride to sodium camphor suspended in the same medium, considerable heat was generated, and a bulky precipitate was produced. The mixture was warmed on the water-bath and left for a few days, after which it was treated with water, when a white precipitate of antimony oxides separated. The toluene

solution which drained from this precipitate was distilled in steam, and the residue extracted with benzene. From the concentrated benzene extract, a substance separated in needles, ice-like crystals, this separation being promoted by the addition of light petroleum. After repeated crystallisation from benzene, the product melted and decomposed at 244°, ultimately when rapidly heated it sometimes remained unchanged at 250°.

0.1314 gave 0.2660 CO_2 and 0.0840 H_2O . $\text{C}=55.21$; $\text{H}=10.0$.

0.1830 " 0.3706 CO_2 " 0.1116 H_2O . $\text{C}=55.3$; $\text{H}=10.77$.

0.2235 " 0.0591 Sb_2S_3 . $\text{Sb}=18.83$.

0.2483 " 0.1196 AgCl . $\text{Cl}=11.02$.

$\text{C}_{30}\text{H}_{40}\text{O}_3\text{ClSb}$ requires $\text{C}=55.90$; $\text{H}=10.0$; $\text{Sb}=18.83$;
 $\text{Cl}=11.02$ per cent.

0.3120, in 25 c.c. chloroform, at 20°, gave $n_D^{20}=1.479$, whence $[\alpha]_D=367.3^\circ$.

Triphenylstibine chloride dissolves only sparingly in alcohol, and is insoluble in water. In acid solutions it is fairly stable, and may be boiled with 2*N*-hydrochloric acid without decomposition. On warming with 2*N*-sodium hydroxide, the chloride was readily hydrolysed into antimonious and hydrochloric acids and camphor. Destructive hydrolysis occurred on warming the chloride with aqueous sodium hydrogen carbonate at 55°, and continued heating with dilute ammonia led to the liberation of camphor. A similar decomposition took place when the chloride was digested with alcoholic silver nitrate.

Triphenylstibine Hydroxynitrate.—0.621 Grams of triphenylstibine chloride gave 0.419 gram of silver chloride (the calculated amount being 0.421 gram) on warming with two molecular proportions of silver nitrate in alcoholic solution. The filtrate, on concentration, furnished white crystals, which, on analysis, gave numbers corresponding with the partial hydrolysis of the initially formed dinitrate. This hydrolysis was brought to a definite end-point by dissolving the white crystals in boiling water; for, on cooling, the hydroxynitrate separated in lustrous, prismatic leaflets, softening at 220°, and melting to a yellow liquid at 225°.

When carrying out the process on a larger scale, any slight excess of silver retained in the solution was precipitated by the addition of sodium chloride. The presence of excess of this salt in the filtrate promoted the crystallisation of the hydroxynitrate, the precipitation, under these conditions, being almost complete.

0.2691 gave 0.4932 CO_2 and 0.0942 H_2O . $\text{C}=50.00$; $\text{H}=3.80$.

0.3765 " 0.1461 Sb_2S_3 . $\text{Sb}=27.72$.

0.3300 gave 9.6 c.c. N_2 at 24° and 759 mm. $N=3.19$.

$C_{18}H_{16}ONbSb$ requires $C=50.23$; $H=3.72$; $Sb=27.9$;

$N=3.26$ per cent.

Triphenylstibine oxynitrate is almost insoluble in cold water, but dissolves readily in alcohol, giving rise to a solution which on standing deposits a very considerable amount without any deposition of stibine oxynitrate taking place. When reduced with Devarda's alloy, it decomposes in the presence of alkali, triphenylstibine is produced, and the whole of the nitrogen is eliminated as ammonia. An estimation of nitrogen by this method gave 3.26 per cent, the calculated value being 3.26 per cent.

Triphenylstibine hydroxyphosphate was prepared by adding an alcoholic solution of triphenylstibine chloride (1 mol.) to a boiling aqueous solution of silver sulphate (2 mols.). The filtrate from the silver chloride was concentrated to remove the alcohol when the hydroxyphosphate separated in colourless nodular crystals, the solution being distinctly acid, owing to the liberation of sulphuric acid.

0.2602 gave 0.0761 H_2SO_4 . $S=4.01$.

$C_{18}H_{16}O_2Sb_2$ requires $S=3.84$ per cent.

The hydroxyphosphate is almost insoluble in cold water; it dissolves in cold concentrated sulphuric acid, and remains in solution after considerable dilution with water, this increase in solubility indicating its conversion into the normal sulphate.

Triphenylstibine hydroxyphosphate melts and decomposes at 252° .

Triphenylstibine hydroxychloride was produced by adding an alcoholic solution of triphenylstibine chloride to a large volume of boiling water and evaporating until crystallisation began. The crystalline deposit when dried and dissolved in benzene, separated from this solvent in transparent, lustrous, colourless spicules, melting at 218° .

0.2982 gave 0.1240 Sb_2S_3 . $Sb=34.0$.

$C_{18}H_{16}OClSb$ requires $Sb=29.73$ per cent.

The authors desire to express their thanks to the Government Grant Committee of the Royal Society for a grant, which has partly defrayed the expenses of this investigation.

ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S.W.

V.—*Experiments on Substituted Allenecarboxylic Acids. Part. I.*

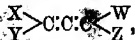
By ARTHUR LAPWORTH and ELKAN WECHSLER

SINCE the appearance of Thiele's papers on the conjugation of unsaturated linkings, an increasing amount of attention has been paid to the question of the mutual influence of points of unsaturation within the molecule, and to the manner in which this influence varies with the relative disposition of these centres of activity.

Thiele has pointed out that the stability of the conjugated system of atoms, $X:Y:Z:W$, is, as a rule, much greater than that of isomeric systems in which the ethylenic and single linkings are not arranged alternately. Such a system therefore has an abnormally small residual affinity, and abnormalities in chemical and physical behaviour are naturally associated with the presence of this structure. It would appear, a priori, not improbable that the system $X:Y:Z$ represents that with the greatest residual affinity; it might therefore be anticipated that any abnormalities displayed by substances containing it would, for the most part, be opposite in sense to those shown by compounds containing the conjugated system; the resulting reactivity of the complex is doubtless the reason why so few allene derivatives have as yet been isolated; and is the most obvious explanation of the circumstance. Instability might be expected to demonstrate itself in isomeric change of the substance at the moment of its formation into an acetylene derivative, or into the isomeric compound with the bonds in the conjugated position, where this is possible, or by the rapid absorption of water or other available reagent. The great activity of the ketens $R_2C:C:O$ is suggestive in connexion with this point. In order that an allene derivative should possess a comparatively high degree of stability, it seemed desirable that isomeric change by the migration of double linkings should, as far as possible, be obviated, and, further, that the residual affinity of the complex should be made as low as possible by associating each of the ethylenic linkings with another centre of unsaturation, so as to introduce the effect of conjugation. Thus it was to be anticipated that the system $C:C:C:C:C$ would have a degree of permanence intermediate between that of a conjugated and a simple allene system.

Some of the effects of conjugation are noticed when an aromatic nucleus or a carbonyl group is directly attached to two doubly

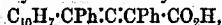
linked atoms, and a quite definite degree of stability might be anticipated in the case of an allene derivative,



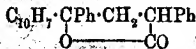
in which X, Y, W, Z are all either aromatic nuclei or carbonyl groups.

With the view of ascertaining how far these extensions of the conceptions of Thiele would apply to such a case, it was decided to attempt the preparation of a substance of this type. Such a substance possesses an interest which is enhanced by the fact that its molecule is built on one of the types shown by van't Hoff to be theoretically capable of exhibiting the phenomenon of enantiomorphous isomerism associated with optical activity, in spite of the circumstance that no asymmetric atom in the strict sense is present. The latter property, it may be pointed out, is not restricted to the case in which the four groups X, Y, W, and Z are all different, but requires only the condition that X is not identical with Y, and W is not the same as Z.

The first substance which the authors sought to prepare was α -diphenyl- γ -1-naphthylallene- α -carboxylic acid,



in which all of those conditions are realised. The method adopted was to proceed from the ester of β -benzoyl- α -phenylpropionic acid, $\text{CH}_3\text{Br}\cdot\text{CHPh}\cdot\text{CO}_2\text{Et}$. This was allowed to react with magnesium α -naphthyl bromide, and, under the conditions finally imposed, gave the lactone:



In the next stage of the process, the lactone was heated with phosphorus pentachloride on the water-bath, and the product poured into absolute alcohol in the anticipation that the chloro-ester would thus be produced, but it was noticed that during this treatment much hydrogen chloride was evolved, indicating that either an unsaturated compound was in process of formation, or that replacement of hydrogen by chlorine was taking place, but the product, however, behaved as a saturated compound. The gummy ester yielded no crystalline material, even after boiling with tertiary bases with the object of removing the hydrogen chloride, but finally it was discovered that, by using rather more than two molecular proportions of phosphorus pentachloride, the product, treated as indicated above, gave a moderately good yield of a crystalline ester, free from chlorine.

The new substance was for a long time thought to be the unsaturated ester, $\text{C}_{10}\text{H}_7\cdot\text{CPh}\cdot\text{CH}:\text{CHPh}\cdot\text{CO}_2\text{Et}$, formed by the

removal of the elements of hydrogen chloride from the chloro-ester above depicted, but the analyses of the pure compound and all its derivatives gave numbers for the hydrogen atoms which were decidedly too low, and the analytical evidence was that the molecules contain two hydrogen atoms less than the monochloro substances directly derived from one having the above structure.

The phosphorus pentachloride had replaced the hydrogen as well as oxygen by chlorine, and doubtless in the case shown with respect to the carbonyl group, so that the necessary amount of at least two molecular proportions of this agent was consumed.*

In view of the concordance of all the analytical results and in spite of certain abnormal properties of some of the derivatives, we have no hesitation in affirming our view that the allene ester has a formula containing two hydrogen atoms less than the number shown in the above structure, and may be regarded as being formed by the removal of two molecules of hydrogen chloride from a dichloro-ester or an unsaturated monochloro-ester.

For a long time the authors were convinced that they had to deal here with phenyldinaphthylallene-carboxylic acid, the synthesis of which they had concerned themselves, but in view of a paper by Vorländer and Siebert (*Ber.*, 1906, 39, 2123), to which their attention was afterwards directed, their confidence is not complete. The communication referred to contains the account of tetraphényllallene, which is formed, instead of tetraphénylacetone, when barium diphenylacetate is heated; the ease with which the allene grouping is formed in this instance illustrates in a clear manner, the effect of the aromatic nucleus upon the point of view discussed in the previous pages. Tetraphényllallene, like some of the unsaturated compounds, but unlike the allene described in the present paper, is stable towards permanganate (in aqueous solution), but is slowly oxidised by chromic acid; on treatment with acids, it yields an isomeric hydrocarbon, in which the allene structure is apparently not present. Further, the original hydrocarbon on bromination yields a monobromo-derivative, and of the isomeric hydrocarbon.

Having regard to the characters and mode of formation of all the substances here described and the work of Vorländer and Siebert, the most probable view seems to be that the ester itself has the allene structure, but that its lactone and the bromo-

* The direct replacement of hydrogen by chlorine when phosphorus pentachloride is used at a temperature at 100° is certainly unusual. Andersen, *Monatsh.*, found that anisole was chlorinated by this agent at 30–70° (*Arch. Pharm.*, 1895, 223, 31), and Titherley and Hicks noticed that phosphorus pentachloride replaces hydrogen by chlorine when it is heated with phenylbenzomexoxazine in chloroform solution at 60° (*Trans.*, 1909, 95, 912).

derivative are perhaps genetically related to the isomeride of tetraphenylallene.

The acid is very readily altered by treatment in alkaline solution with sodium amalgam, and although the reduction product has never been obtained in crystalline form, this property of the acid is probably an $\alpha\beta$ -unsaturated acid.

It was readily converted into a lactone on treatment with mineral acids, so that it is probably a $\beta\gamma$ -unsaturated acid. Further, the lactone thus obtained is not identical with the saturated lactone from which it was originally prepared, nor does it contain a detectable quantity of the very characteristic substance.

On the other hand, the acid and its salts only absorb one molecular proportion of bromine, yielding a monobromide lactone; this exhibits great stability, and resists for some time the action of hot permanganate solution.

The acid is difficult to form a very stable, crystalline substance, from which the other is only removed with difficulty even by distillation. The salts which the acid forms with bases, however, show little tendency to crystallise; the salts with alkalis behave differently, the compounds of the acid with all the organic bases and alkaloids experimented with, piperidine excepted, did not yield any trace of crystalline salt.

Other methods applicable for resolving acids into their enantiomorphous constituents were tried, but in all cases without definite results.

The acids are presented in their present form, as the authors are no longer able to work in collaboration.

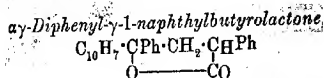
EXPERIMENTAL

In preparing the β -benzoyl- α -phenylpropionitrile required for the investigation the process described by Hann and Lapworth (Trans., 1904, 85, 1368) was found to be tedious and wasteful of alcohol when large quantities of material were dealt with. After a considerable number of experiments, the following modified process was found to give excellent results.

A solution of benzylideneacetophenone (23.4 grams) in 120 c.c. of 96 per cent alcohol and 30 c.c. of glacial acetic acid was warmed to 50° and into this was then introduced, by means of a test-tube drawn out at the top to a coarse capillary which rested on the bottom of the flask, a solution of potassium cyanide (15 grams) in 25 c.c. of water. The temperature was maintained at 50–55° for a further fifteen minutes, when crystals of the nitrile were added, and the vessel was then cooled by a stream of cold water. The

deposited solid, which was obtained in nearly theoretical quantity, was purified by crystallisation from alcohol.

The following modified process was used in crystallising the nitrile. Ten grams of the finely powdered compound were shaken with a mixture of 50 grams of sulphuric acid and 50 grams of water, at the temperature of the water-bath, until dissolved, and the whole was subsequently allowed to remain on the water-bath several hours. After cooling, the cake of impure acid formed was separated, washed, and purified as before (*loc. cit.* p. 381). The preparation of the ethyl ester was effected by warming the dry acid with half its weight of sulphuric acid and ten times its weight of alcohol for several hours, the liquid being then poured into a large bulk of water, which was afterwards shaken with an equal bulk of light petroleum. After filtration, the fluids separate rapidly, and the petroleum solution, after being washed with dilute sodium carbonate solution, dried, and evaporated, deposits the ester in magnificent crystals.



Magnesium α -naphthyl bromide in ethereal solution was prepared in the usual manner, and added to a solution containing one molecular proportion of ethyl β -benzoyl- α -phenylpropionate in about twenty times its weight of benzene. The solution was not cooled during this process, as it was found that a much better yield of the desired product was thus obtained, owing probably to the fact that the solution, if cooled, deposited a viscid oil, which tended to carry down with it much of the unaltered ester. At the end of the operation the solution was freed from magnesium compounds in the usual manner, and the ether and benzene were afterwards removed by the use of a current of steam. The residual viscid mass was separated from the water and dissolved in hot acetone, the crystals which separated on cooling being removed at the end of twenty-four hours, and recrystallised fresh from a mixture of acetone and alcohol, and finally from glacial acetic acid:

0.4812 gave 1.5022 CO_2 and 0.2443 H_2O . C = 85.14; H = 5.64.

$\text{C}_{26}\text{H}_{20}\text{O}_2$ requires C = 85.71; H = 5.49 per cent.

The substance is insoluble in water, only very sparingly soluble in boiling methyl and ethyl alcohols, ether, or light petroleum; it is fairly soluble in carbon disulphide, and readily so in glacial acetic acid, acetone, chloroform, carbon tetrachloride, or benzene. It separates from acetone in colourless, transparent prisms, containing acetone of crystallisation, melting at about

90° (when rapidly heated) to a colourless liquid, from which the acetone rapidly evaporates, leaving a white, crystalline solid, which, on further heating, melts at 166°. The substance, when obtained by crystallisation from hot glacial acetic acid, is free from acetone and melts at 166°.

This lactone dissolves very slowly in boiling aqueous alkalis, but more rapidly in the presence of alcohol. On evaporating the solution or on adding sodium hydroxide, the sodium salt separates as a voluminous, white, gelatinous mass. The cold aqueous solution of the sodium salt, on addition of hydrochloric acid, deposits the hydroxy-acid as a white, amorphous precipitate; this may be extracted with ether, in which it dissolves readily. A crystalline substance rapidly separates when the ethereal extract is allowed to evaporate, but this, on examination, is found to be identical with the original lactone. Owing to the ease with which lactone formation takes place, it is probably not possible to isolate the free acid in a state of purity; the substance precipitated from the solution of the sodium salt consists, nevertheless, of the hydroxy-acid and not of the lactone, for the freshly precipitated substance is readily soluble in dilute aqueous sodium carbonate and in ether, whereas the lactone is insoluble in the former, and but slightly soluble in the latter.

Action of Phosphorus Pentachloride on α -Diphenyl- γ -Naphthyl-butylolactone.

On heating an equimolecular mixture of the lactone and phosphorus pentachloride on the water-bath, the mass gradually melts to a brownish-red liquid, and a considerable quantity of hydrogen chloride is evolved. Several experiments were made with different preparations which had been recrystallised from various solvents and thoroughly dried, but in no case was the evolution of hydrogen chloride affected; even on employing a cold solution of phosphorus pentachloride in chloroform, a considerable evolution of hydrogen chloride was observed. With the object of isolating the corresponding chloro-ester, a mixture of the lactone (10 grams) with phosphorus pentachloride (8 grams) was heated in the water-bath until the evolution of hydrogen chloride had entirely ceased; the resulting liquid was then poured into about 100 c.c. of absolute alcohol, and heated to boiling for about one hour. The next day the alcoholic liquid was diluted with water, neutralised with sodium carbonate, and extracted with ether. A yellowish-brown, resinous oil was then obtained, which, on cooling, set to a hard, transparent, glassy mass. All attempts to prepare a crystalline product from

this by treatment with solvents were unsuccessful; it was therefore dried at 100° for about ten hours, and then analysed.

0.1969 gave 0.9336 AgCl. $\text{Cl} = 4.2$.

$\text{C}_{20}\text{H}_{20}\text{O}_2\text{Cl}$ requires $\text{Cl} = 8.3$ per cent.

The product analysed evidently consisted of a mixture of a chlorinated substance and an unchlorinated substance in roughly equal amounts. This material did not absorb chlorine in the presence of sodium acetate, nor did it decolorise an acidified solution of potassium permanganate even on boiling.

Ethyl α , β -Diphenyl- γ -naphthylallene-carboxylate

$\text{C}_{24}\text{H}_{18}\text{CPh}_2\text{CO}_2\text{Et}$

The impure chloro-ester readily loses hydrochloric acid on boiling with pyridine or quinoline; the reaction, however, takes place much more smoothly with the former, and it is not even necessary to boil the mixture, heating on the water-bath for a few minutes being quite sufficient.

In the first experiments, in which the chloro-ester prepared from an equimolecular mixture of lactone and phosphorus pentachloride was employed, many fractional crystallisations were required before pure unsaturated ester was obtained, and the yield was poor.

Better results were obtained as the proportion of phosphorus pentachloride to lactone in the preparation of the chloro-ester was increased, and after a number of experiments had been made, in which these substances were employed in varying proportions, the following method was finally adopted. The chloro-ester is prepared by heating the lactone (1 mol.) with phosphorus pentachloride (2 mols.), and the product of subsequent decomposition with alcohol is heated with twelve times its weight of pyridine for three hours on the water-bath, and then to boiling for a few minutes. After cooling, the liquid is mixed with about twice its volume of ether, and extracted with hydrochloric acid until the pyridine is completely removed. The ethereal liquid is then washed and distilled, and the residue crystallised from boiling alcohol.

The yield amounts to about one-half of the weight of lactone employed. The substance was purified by recrystallisation from glacial acetic acid and alcohol.

0.1964 gave 0.1000 H_2O and 0.6191 CO_2 . $\text{C} = 85.97$, $\text{H} = 5.64$.

$\text{C}_{22}\text{H}_{18}\text{O}_2$ requires $\text{C} = 85.71$, $\text{H} = 5.61$ per cent.

$\text{C}_{22}\text{H}_{20}\text{O}_2$ „ $\text{C} = 85.15$, $\text{H} = 5.94$ „

The substance is readily soluble in hot alcohol, from which it separates almost completely on cooling in stellar aggregates of colourless needles, which turn yellow on heating, and melt at

118.5°. It is readily soluble in acetone, glacial acetic acid, benzene, chloroform, or carbon tetrachloride, and sparingly so in methyl alcohol and petroleum. A solution of the substance in glacial acetic acid quickly discharges the colour of bromine even in the presence of sodium acetate.

Diethyl 2,4-diphenylallene-carboxylic Acid.



The acid (2.2 grams) was heated on the water bath with a mixture of 10 c.c. of *N*-sodium hydroxide and 100 c.c. of pyridine during the night. The liquid was then diluted considerably with water, stirred until the pyridine was completely removed, cooled, and decomposed with dilute acetic acid. The new acid which separated was a very voluminous, gelatinous, white precipitate, was collected, washed, and dried on porous porcelain. The substance was then extracted with a small quantity of ether, in which it readily dissolves, but separates again almost instantly in the form of a dense, white, fluffy mass; at the same time a considerable quantity of ether-insoluble acid, and this always adheres to the amorphous acid, was left after drying on porous porcelain for several days. The substance can be purified by crystallisation from boiling ether, when it is obtained, on cooling, in the form of large, colourless, transparent, highly refractive, rhombic crystals, which contain ether on crystallisation. For the purification of quantities exceeding one gram it is expedient to carry out the extraction in a Soxhlet apparatus, owing to the very slight solubility of the substance in ether.

For the determination of the ether of crystallisation, a weighed quantity was heated in a vacuum in a tube immersed in boiling xylene until the weight remained constant.

0.5638 lost 0.0952. $\text{C}_{20}\text{H}_{16}\text{O}_4 = 16.87\%$

0.4848 required 11.2 c.c. *N*/10-sodium hydroxide for neutral-

isation. Equivalents = 432.

$\text{C}_{20}\text{H}_{16}\text{O}_4 \cdot \text{H}_2\text{O}$ requires $\text{C}_{20}\text{H}_{16}\text{O}_4 = 16.97\%$ per cent.

0.5638 lost 0.0952. Equivalents = 436.

In the preparation of the ether-free acid for analysis, a portion of the ether-containing crystals was dissolved in ammonia, the solution was filtered, the ether cooled, and acidified with hydrochloric acid. The precipitated acid was collected and dried at 100°, and finally purified by crystallisation from benzene:

0.2387 gave 0.545 CO_2 and 0.1117 H_2O . $\text{C} = 86.2$; $\text{H} = 5.2$.

0.2474 „ 0.7809 CO_2 „ 0.1103 H_2O . $\text{C} = 86.1$; $\text{H} = 4.95$.

$\text{C}_{20}\text{H}_{16}\text{O}_4$ requires $\text{C} = 86.19$; $\text{H} = 4.97$ per cent.

The pure acid can also be readily obtained by crystallising the ether-containing acid from boiling anisole. A portion prepared in this manner was titrated:

0.4830 required 13.4 c.c. *N*/10-sodium hydroxide. Equivalent = 360.

$C_{26}H_{18}O_2$ requires Equivalent = 362.

The acid is slightly soluble in boiling ether, but much less so in cold ether. The ether-containing crystals melt only when heated rapidly, the ether evaporating, and the substance then solidifying; on further heating, the substance changes colour at about 180°, and melts indefinitely at 185–193°. The acid is readily soluble in acetone or glacial acetic acid, and fairly soluble in benzene, chloroform, or alcohol. It is insoluble in water, but dissolves in dilute aqueous alkalis. On adding sodium hydroxide to a solution of the sodium salt, a white, gelatinous precipitate separates even from very dilute solutions. The acid decolorises a solution of bromine in glacial acetic acid, and an aqueous solution of the sodium salt reacts at once with cold potassium permanganate.

Attempts to Resolve the Acid.

A number of attempts were made to prepare crystalline salts of the acid with the following active bases: quinine, strychnine, brucine, narcotine, cinchonine, cocaine, coniine, aminocamphor, nicotine, and menthylamine. Mixtures of acid and base in suitable organic solvents, such as ether, alcohol, acetone, and chloroform, under varying conditions, in no case gave any crystalline salts. In many instances crystals were deposited, but these were invariably found to consist either of the unchanged acid or base. An attempt was also made to resolve the acid by treating an alcoholic solution with one-half an equivalent of sodium ethoxide and one-half an equivalent of coniine, and fractionally precipitating the coniine salt by successive additions of water. The acids isolated from the various fractions were all found to be inactive.

An attempt was also made to prepare the menthyl ester by heating the acid with menthol, and also the conide by heating the ester with coniine, but, although interaction occurred, no trace of any crystalline material could be isolated from the neutral gummy products.

Formation of the Unsaturated Bromolactone, $C_{26}H_{16}O_2Br$.

An acetic acid solution of the ester rapidly absorbs bromine, even in the presence of sodium acetate. Titration of the ester with a standardised solution of bromine in glacial acetic acid, employing

potassium iodide as external indicator, proved that one molecule of ester reacts with two atoms of bromine. For the preparation of the bromine compound, a solution of the ester (2 grams) in glacial acetic acid (20 cc.) was mixed with sodium acetate (1 gram), and then with a 10 per cent. solution of bromine in glacial acetic acid (8.16 cc.). After some minutes, water was added, when the bromine compound separated as a white, crystalline precipitate. This was collected, washed, and dried, then twice crystallised from boiling glacial acetic acid, washed with alcohol, and dried at 100° :
 0.2975 gave 0.7683 CO_2 and 0.1029 H_2O . $\text{C}=70.43$; $\text{H}=3.84$.
 0.3106 " 0.8041 CO_2 " 0.1086 H_2O . $\text{C}=70.62$; $\text{H}=3.88$.
 0.3349 " 0.8660 CO_2 " 0.1159 H_2O . $\text{C}=70.76$; $\text{H}=3.80$.
 0.2525 " 0.1064 AgBr. Br=17.92.
 $\text{C}_{20}\text{H}_{18}\text{O}_2\text{Br}$ (unsaturated bromolactone) requires $\text{C}=70.75$;
 $\text{H}=3.85$; Br=18.14 per cent.*

The substance is fairly soluble in boiling glacial acetic acid, from which it separates on cooling in slender, colourless needles, which melt on heating at 192° . It is only very sparingly soluble in alcohol, ether, or benzene, almost insoluble in light petroleum, but fairly readily soluble in boiling acetone or chloroform. It does not decolorise a solution of bromine in glacial acetic acid or a solution of potassium permanganate in acetone.

Action of Mineral Acids on the Unsaturated Carboxylic Acid.

On heating a solution of diphenylnaphthylallenecarboxylic acid in glacial acetic acid, to which a few drops of concentrated hydrochloric acid have been added, a white, crystalline powder separates. The mixture was heated on the water-bath until no further separation took place (about one hour), the crystalline precipitate was then collected, and crystallised from boiling glacial acetic acid:

0.2375 gave 0.7474 CO_2 and 0.1094 H_2O . $\text{C}=85.83$; $\text{H}=5.11$.

$\text{C}_{26}\text{H}_{18}\text{O}_2$ requires $\text{C}=86.16$; $\text{H}=4.97$ per cent.

The substance is readily soluble in acetone, glacial acetic acid, benzene, chloroform, or ethyl acetate, sparingly so in boiling alcohol, but almost insoluble in the cold. It does not decolorise an acetone solution of potassium permanganate even on boiling. It does not dissolve appreciably in boiling aqueous sodium carbonate or sodium hydroxide, and is only very slowly attacked by boiling ethyl- or amyl-alcoholic sodium hydroxide. It is reduced on adding sodium or sodium amalgam to the hot amyl-alcoholic solution. In both cases, however, all attempts to isolate a

* $\text{C}_{28}\text{H}_{22}\text{O}_2\text{Br}$ (bromo-ester) requires $\text{C}=71.34$; $\text{H}=4.88$. Br=16.98.

$\text{C}_{26}\text{H}_{18}\text{O}_2\text{Br}$ (bromo-lactone) " $\text{C}=70.41$; $\text{H}=4.32$. Br=18.05.

crystalline substance from the reduction product were unsuccessful, and no indication could be obtained of the formation of the saturated lactone or of the hydroxy-acid corresponding with it.

Some of the expense of this work was defrayed by the aid of a Government grant from the Royal Society for which the authors desire to express their thanks.

GOLDSMITHS' COLLEGE, NEW CROSS, S.E.

VI.—The Production of para-Diazoimides from Alkyl- and Aryl-sulphonyl-para-diamines, and the General Reaction.

By GILBERT T. MORGAN and JOSEPH A. PICKARD, B.Sc., and C.S.

CERTAIN derivatives of *p*-phenylenediamine give rise to diazonium salts, from which diazoimines or diazoimides may be produced by internal condensation. The earliest known *p*-diazoimine is the explosive phenyl-*p*-diazoiminobenzene, $C_6H_5 \cdot N \cdot C_6H_4 \cdot N$, discovered by Ikuta (*Annalen*, 1888, **243**, 282), and afterwards prepared by Hantzsch (*Ber.*, 1902, **35**, 895). In 1904, one of us, in conjunction with F. M. G. Micklethwait, obtained the first *p*-diazoimide from camphor- β -sulphonyl-*p*-phenylenediamine (*Trans.*, 1905, **87**, 1374), and subsequently showed that benzenesulphonyl-*p*-phenylenediamine and its homologues readily yield arylsulphonyl-*p*-phenylenediazoimides (*Trans.*, 1905, **87**, 921, 1302).

Although these diazoimides are moderately stable substances, yet comparative experiments proved that they and Ikuta's unstable diazoimine are members of the same class of diazo compounds. This relationship was demonstrated by the preparation of a connecting series of mono-, di-, and tri-nitrophenyl-*p*-phenylenediazoimines, the stability of which increases as nitro-groups are introduced successively into the molecule of *p*-aminodiphenylamine (*Trans.*, 1908, **93**, 605).

These *p*-diazoimines and *p*-diazoimides are distinguished from the *o*-diazoimines and *o*-diazoimides by their intense colour, generally either yellow or orange, and by their very reactive character. When treated with cold concentrated mineral acids, they regenerate the corresponding diazonium salts, and with phenols and aromatic amines they couple additively to form azo-derivatives. On account of these properties, some of the more readily prepared

members of the group can be turned to account in the production of azo-colouring matters (*J. Soc. Dyers*, 1909, 25, 107).

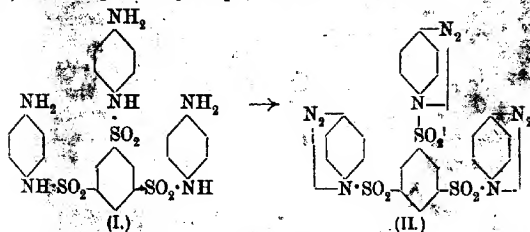
These results render plausible the view that the property of forming *p*-diazoino compounds is possessed by all derivatives of *p*-phenylenediamine having the formula $\text{RNH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, and even by the base itself, but more experimental evidence would be required before it could be definitely stated that the reaction is a perfectly general one.

By the experiments described in the present communication we have endeavoured to show that, in all probability, the reaction is general for all organic sulphonyl derivatives of *p*-phenylenediamine. This demonstration may be conveniently divided into three stages.

I.—*Para-diazoimides Containing Arylpolysulphonyl Groups.*

The conversion of benzene-1:3-disulphonylbis-*p*-phenylenediamine into the corresponding bis-diazoimide has already been accomplished (Trans., 1905, 87, 1309), and, in the present instance, the case of benzene-1:3:5-trisulphonylter-*p*-phenylenediamine (I) has been examined as a typical example of an amide derived from a complex polysulphonic acid.

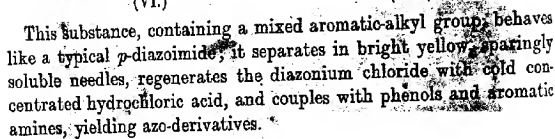
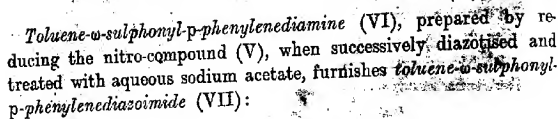
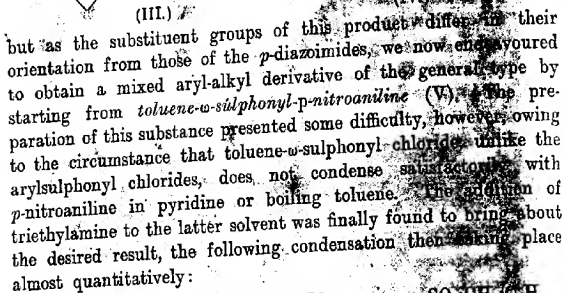
Apart from certain practical difficulties encountered in the preparation of the triamine, it was found that the conversion of this base into benzene-1:3:5-trisulphonylter-*p*-phenylenediazoimide (II) is a comparatively simple matter:



This result justifies the conclusion that the production of the diazoimide is independent of the number of sulphonyl groups present in the molecule of the aromatic aminosulphonamide.

II.—*Para-diazoimides Containing Mixed Aryl-alkylsulphonyl Groups.*

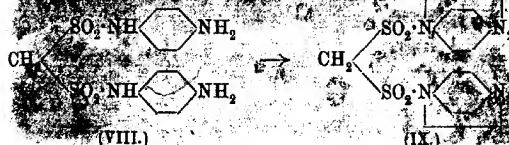
Former experiments on the constitution of diazoimides led to the interesting observation that *o*-benzenesulphonyl-*o*-benzylene-
VOL. XCVII, E



The existence of camphor-8-sulphonyl-7-phenylenediazoimide (*loc. cit.*) shows that the presence of an aromatic group attached to the sulphur atom is not an essential condition for the formation of a diazoimide of this type, and accordingly we took steps to obtain diazoimino-derivatives containing the simplest alkylsulphonyl groups.

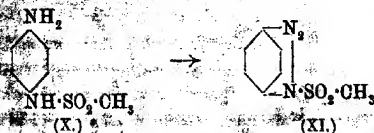
Methionie chloride condenses readily with *p*-nitroaniline, yielding *methanesulphonylbis-p-nitroaniline*, $\text{CH}_2(\text{SO}_2\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$, which, on reduction, gives rise to *methanesulphonylbis-p-phenylenediamine* (VIII), an amphoteric substance, yielding both a sodium derivative and a dihydrochloride. The latter compound, when diazotised, furnishes a fairly stable *bisdiazonium chloride*, the colourless solution of which turns yellow on the addition of aqueous sodium acetate, thus indicating the formation of a diazoimide.

Methanesulphonylbis-p-phenylenediazoimide (IX) is, however, isolated only when either the dry diazonium chloride is dusted into concentrated aqueous sodium acetate, or when crystals of this salt are added to a strong solution of the diazonium compound:



This diazoimide has the physical and chemical properties which characterise the group, but is less stable than the more complex members. It is somewhat soluble in water, although the solubility is considerably diminished in the dried specimens.

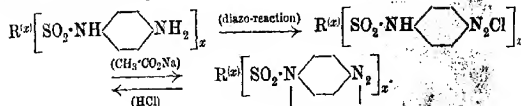
The production of the simplest possible alkylsulphonyl-*p*-phenylenediazoimide has been accomplished by the following series of operations. *Methanesulphonyl-p-nitroaniline*, produced by condensing methanesulphonyl chloride and *p*-nitroaniline in the presence of triethylamine, yields, on reduction, *methanesulphonyl-p-phenylenediamine* (X). The diazonium chloride and sulphate of this base are colourless salts, which give yellow solutions of the diazoimide on treatment with sodium acetate:



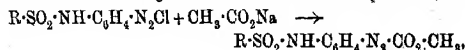
Methanesulphonyl-p-phenylenediazoimide (XI) is soluble in water, and as it rapidly decomposes into a resinous product even in cold aqueous solutions, its isolation in the solid state is a matter of considerable difficulty. When silver nitrite is introduced into a solution of methanesulphonyl-*p*-phenylenediamine hydrochloride, silver chloride is precipitated, and the solution then contains only the diazoimide, which may be obtained by evaporating to dryness

in a vacuum over phosphoric oxide. Unless this evaporation is effected very rapidly, the product darkens, and some loss of nitrogen is apparent. When sodium nitrite is used in this experiment, the filtered solution contains molecular proportions of the diazoimide and sodium chloride. The presence of this inorganic salt seems to increase the stability of the diazoimide, and the solution may be evaporated to dryness in a vacuum without loss of nitrogen.

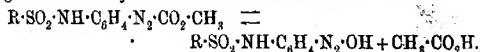
With the production of the two foregoing diazoimides, containing respectively methanesulphonyl and methanedisulphonyl groups, the task of demonstrating the general character of this chemical change is completed, and the reaction may be expressed in general terms in accordance with the following symbolical scheme, where R is any alkyl, aromatic, hydroaromatic, or mixed aromatic-alkyl radicle, and x is its valency:



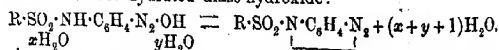
The conversion of the diazonium chloride into the *p*-diazoimide is a reversible change, and it is of interest, in connexion with the modern theories of solution, to notice that the reaction probably occurs in three or more successive phases. The inverse change is brought about, not only by mineral acids, but even by acetic acid when present in excess, and this result indicates that the first phase in the direct change is the formation of a diazonium acetate:



which, in the absence of any considerable excess of free acetic acid, undergoes hydrolysis, the extent to which this second phase occurs being determined by the concentration of the acetic acid:



The hypothetical diazo-hydroxide thus produced is an amphoteric substance, having an acidic substituent, $\text{R} \cdot \text{SO}_2 \cdot \text{NH}$, and a basic group, $\text{N}_2 \cdot \text{OH}$, each of which probably exists in solution in association with a certain characteristic number of water molecules. But as the sodium acetate solution invariably assumes the yellow colour of the *p*-diazoimide, one must suppose that a certain proportion of this substance is actually formed in solution by the internal condensation of the hydrated diazo-hydroxide:



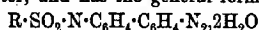
This mode of representing the final phase of the condensation is

probably true only when R is a complex group of comparatively high molecular weight. In these cases, the precipitation of the *p*-diazoidime is immediate and practically complete, but when R is a simple alkyl group of low molecular weight, the *p*-diazoidime exhibits a tendency to remain in solution, probably in the hydrated form:



Methanesulphonyl-*p*-phenylenediazoidime is obtained only on evaporating its solution to dryness under greatly reduced pressure, and methanedisulphonylbis-*p*-phenylenediazoidime in the moist condition dissolves fairly readily in cold water, and becomes much less soluble only after desiccation over phosphoric oxide.

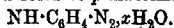
Further evidence for the existence of hydrated forms of the diazoidimes was obtained by F. M. G. Micklethwait, J. M. Hird, and one of us in the study of the arylsulphonylbenzidines. In these bases, where the acid and basic substituents are separated by two aromatic nuclei, the diazoidime separates with two molecular proportions of water, and has the general formula:



(Trans., 1907, **91**, 1509; 1908, **93**, 615).

The closely allied aromatic diazo-oxides exhibit the same phenomenon; the more complex members of the series separate in anhydrous forms, as, for example, dinitrophenylenediazo-oxide, $\text{O} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{N}_2$, whereas Hantzsch and Davidson (*Ber.*, 1896, **29**, 1530) found that the simplest member, *p*-phenylenediazo-oxide, separates with four molecules of water, and can be represented by the formula $\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot 4\text{H}_2\text{O}$.

In connexion with the existence of hydrated forms of diazoidimes, attention should be directed to an interesting observation made by the chemists of the Badische Anilin- und Soda-Fabrik (D.R.-P. 205037). Acetyl-*p*-phenylenediamine was diazotised in hydrochloric acid, and the acetyldiazonium chloride hydrolysed by gently heating the solution. The dissolved product was then found to couple with alkaline β -naphthol much less rapidly than the unhydrolysed acetyl-*p*-aminobenzenediazonium chloride. Although the product of hydrolysis was not isolated, it seems probable that it consists of a hydrated form of *p*-diaziminobenzene,



EXPERIMENTAL.

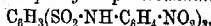
I.—Benzene-1: 3: 5-trisulphonylter-*p*-phenylenediamine.

A mixture of benzene-1: 3: 5-trisulphonyl chloride (1 mol.) and *p*-nitroaniline, (3 mols.) was boiled in dry pyridine for several hours, the solvent then removed by evaporation, and the residue, after extraction with water, was boiled with aqueous sodium carbonate. The alkaline filtrate, when acidified with dilute hydrochloric acid, yielded a yellowish-white precipitate, which after repeated crystallisation from methyl alcohol, separated as a white, crystalline powder, and melted at 278°:

0.2202 gave 23.6 c.c. N_2 at 17° and 758.2 mm. $N = 12.58$.

0.2100 „ 0.2162 $BaSO_4$. $S = 14.15$.

$C_{24}H_{18}O_{12}N_6S_6$ requires $N = 12.40$; $S = 14.19$ per cent.

Benzene-1: 3: 5-trisulphonylter-*p*-nitroaniline,

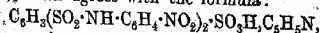
is a distinctly acidic substance, and on treatment with alcoholic potash gives a potassium derivative, separating in small yellow crystals.

When diluted with an equal volume of water, the methyl-alcoholic mother liquors of the preceding compound deposited a brown oil, which gradually solidified to radiating clusters of stout, yellow prisms. This product, when washed with cold ethyl acetate and crystallised from alcohol, was obtained in odourless, yellow crystals; insoluble in water or dilute hydrochloric acid, but dissolving in cold aqueous sodium hydroxide to a yellow solution having a strong odour of pyridine:

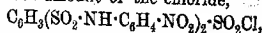
0.1288 gave 12.8 c.c. N_2 at 24° and 763 mm. $N = 11.19$.

$C_{23}H_{19}O_{11}N_5S_5$ requires $N = 11.01$ per cent.

This result, which agrees with the formula:

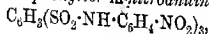


shows that a certain amount of the chloride,



arises from the interaction of *p*-nitroaniline and benzene-1: 3: 5-trisulphonyl chloride, the subsequent action of water in the presence of pyridine leading to the production of the above pyridine salt.

A comparative experiment made with the other nitroanilines showed that the ortho-base gave only a small yield of crystalline product with benzene-1: 3: 5-trisulphonyl chloride, whereas the meta-base reacted readily and quantitatively in boiling pyridine to form the following compound.

Benzene-1: 3: 5-trisulphonylter-*m*-nitroaniline,

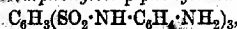
separated from pyridine by removing the latter with cold dilute hydrochloric acid, was crystallised from 50 per cent. acetic acid, and thus obtained in small, white needles, melting at 199° .

0.2657 gave 27.4 c.c. N_2 at 14° and 767.4 mm. $N=12.28$.

$C_{12}H_{10}O_4N_6S_3$ requires $N=12.40$ per cent.

The trisulphonamide is readily soluble in aqueous alkali hydroxides or glacial acetic acid.

Benzene-1:3:5-trisulphonylter-p-phenylenediamine,



was prepared by adding iron filings (10 grams) to benzene-1:3:5-trisulphonylter-p-nitroaniline suspended in 100 c.c. of warm water containing 1 c.c. of glacial acetic acid, the mixture being heated for three hours. Excess of sodium bicarbonate was added, the mixture filtered, and the filtrate acidified with acetic acid, when the triamine separated, the yield being about 50 per cent. When crystallised from water or acetone, the triamine separated in colourless nodules, and melted at 256° .

0.1580 gave 19.5 c.c. N_2 at 23° and 775 mm. $N=14.56$.

$C_{12}H_{10}O_4N_6S_3$ requires $N=14.29$ per cent.

The diazo-solution from 1 gram of base, 30 c.c. of 2*N*-hydrochloric acid, and 20 per cent. sodium nitrite solution was treated with aqueous sodium acetate until a slight permanent precipitate was formed. From the filtered solution, excess of sodium acetate deposited the diazoimide as a light yellow, microcrystalline precipitate, which was washed successively with cold water, alcohol, and ether. The product retained water very tenaciously, its weight becoming constant only after prolonged drying over sulphuric acid or phosphoric oxide:

0.1923 gave 0.3244 CO_2 and 0.0502 H_2O . $C=45.99$; $H=2.70$.

0.1988 „ 34.8 c.c. N_2 at 18° and 757.3 mm. $N=19.75$.

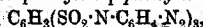
0.2012 „ 0.2235 $BaSO_4$. $S=15.26$.

$C_{12}H_{10}O_6N_6S_3$ requires $C=46.37$; $H=2.43$; $N=20.32$;

$S=15.46$ per cent.

The filtrate from the diazoimide gave a red coloration with alkaline *B*-naphthol, showing that the precipitation of the condensation product was not complete even in the presence of considerable excess of sodium acetate.

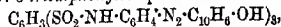
Benzene-1:3:5-trisulphonylter-p-phenylenediazoimide,



which explodes somewhat violently at 146° , is too insoluble to be crystallised from the ordinary organic solvents; it can be preserved for an indefinite time in the dark, although on exposure to light it rapidly darkens and assumes a purple-brown colour. When

dissolved in cold hydrochloric acid, the diazoimide is converted into diazonium chloride, as may be shown by adding the diluted solution to alkaline β -naphthol.

Benzene-1: 3: 5-trisulphonylter-p-aminobenzeneazo- β -naphthol,



obtained either in the preceding reaction or by triturating the diazoimide with β -naphthol in the presence of pyridine, separated from alcohol as a dark red, crystalline powder, melting at 265–266°:

0.1060 gave 10.4 c.c. N_2 at 21.5° and 762 mm. $\text{N}=11.39$.

$\text{C}_{33}\text{H}_{45}\text{O}_9\text{N}_9\text{S}_9$ requires $\text{N}=11.92$ per cent.

This azo- β -naphthol dissolves in concentrated sulphuric acid to a deep red solution; its alkali salts are sparingly soluble in water containing alkali hydroxides, and are decomposed by dilute acetic acid.

II.—*Toluene- ω -sulphonyl-p-phenylenediazoimide,*

It was not found possible to condense *p*-nitroaniline and toluene- ω -sulphonyl chloride in boiling toluene, and in warm pyridine these substances interacted to form tarry products. The difficulty was overcome by dissolving molecular proportions of *p*-nitroaniline, toluene- ω -sulphonyl chloride, and triethylamine in toluene, the liquids being first carefully dried over sodium. After boiling for two to three hours, the condensation was complete, and the solvent was then removed by evaporation. The residue was extracted repeatedly with boiling aqueous sodium carbonate, and the solution filtered while hot. On cooling, the sparingly soluble orange sodium derivative, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{NNa}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, separated; this was decomposed at 0° with dilute hydrochloric acid, when the *toluene- ω -sulphonyl-p-nitroaniline*, which first appeared as a pasty, yellow mass, slowly solidified, and was crystallised from alcohol and water (1:4):

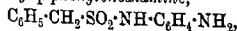
0.1452 gave 12.5 c.c. N_2 at 15° and 737 mm. $\text{N}=9.82$.

0.1075 „ 0.0868 BaSO_4 . $\text{S}=11.09$.

$\text{C}_{15}\text{H}_{12}\text{O}_4\text{N}_2\text{S}$ requires $\text{N}=9.60$ and $\text{S}=10.96$ per cent.

After repeated crystallisation from dilute alcohol, the sulphonamide melts at 155°.

Toluene- ω -sulphonyl-p-phenylenediamine,



was produced in almost quantitative yield by reducing the preceding nitro-compound (4 grams) with iron filings (5 grams) in 100 c.c. of 4 per cent. acetic acid. After boiling for thirty minutes, the mixture, rendered alkaline with sodium carbonate, was filtered, when the filtrate deposited white crystals of the base, a further quantity being extracted from the residue with alcohol. After

crystallisation from this solvent, the base was obtained in acicular prisms, melting at 121—122°:

0.1241 gave 11.8 c.c. N_2 at 16° and 753.5 mm. $N=11.20$.

$C_{13}H_{14}O_2N_2S$ requires $N=10.69$ per cent.

This diamine was diazotised in 6 per cent. hydrochloric acid, and the filtered solution treated with excess of aqueous sodium acetate. The liquid became yellow, and subsequently deposited lemon-yellow needles of the diazoimide. These were washed successively with cold water, alcohol, and ether. The aqueous filtrate gave only a slight coloration with β -naphthol, showing that the precipitation of diazoimide was complete. The product, a typical diazoimide, darkened at 136°, and decomposed violently at 141°:

0.1463 gave 0.3061 CO_2 and 0.0567 H_2O . $C=57.05$; $H=4.31$.

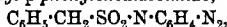
0.1136 „ 15.9 c.c. N_2 at 18° and 735 mm. $N=15.63$.

0.1279 „ 0.1056 $BaSO_4$. $S=11.33$.

$C_{13}H_{11}O_2N_2S$ requires $C=57.14$; $H=4.03$; $N=15.38$;

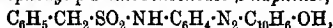
$S=11.73$ per cent.

Toluene- α -sulphonyl- p -phenylenediazoimide,



like the arylsulphonyldiazoimides, is practically insoluble in the ordinary solvents, but dissolves in cold hydrochloric acid, regenerating the diazonium chloride. Although stable in the dark, it rapidly darkens on exposure to light, becoming orange, and finally dark brown.

Toluene- α -sulphonyl- p -aminobenzeneazo- β -naphthol,



prepared either by triturating the diazoimide with β -naphthol and pyridine, or by adding the acid solution of the diazoimide to alkaline β -naphthol, separated from alcohol as a bright red, crystalline powder, melting at 211°:

0.2110 gave 19 c.c. N_2 at 12° and 763 mm. $N=10.68$.

$C_{23}H_{19}O_3N_3S$ requires $N=10.10$ per cent.

[With F. M. G. MICKLETHWAIT.]

III.—*Methanedisulphonylbis- p -phenylenediazoimide.*

When methionie chloride* (1 mol.) and p -nitroaniline (2 mols.) were mixed in dry toluene, a vigorous reaction took place, and the condensation was completed by warming the mixture for a few minutes. After removing the toluene by evaporation, the residue

* For the specimen of methionie chloride employed in the following experiments, we are indebted to the liberality of the Farbenfabriken vormals Friedrich Bayer & Co.

was extracted successively with boiling water to remove *p*-nitroaniline, and with aqueous sodium carbonate to dissolve the *methanedisulphonylbis-p*-nitroaniline, $\text{CH}_2(\text{SO}_2\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$. The latter substance was then crystallised from alcohol, when it separated in transparent, light yellow prisms, melting and decomposing at 248—249°:

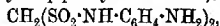
0.1607 gave 19.0 c.c. N_2 at 25° and 774 mm. $\text{N}=13.54$.

0.1871 „ 0.2216 BaSO_4 . $\text{S}=16.27$.

$\text{C}_{13}\text{H}_{10}\text{O}_8\text{N}_4\text{S}_2$ requires $\text{N}=13.48$; $\text{S}=15.41$ per cent.

Methanedisulphonylbis-p-nitroaniline decomposes both soluble and insoluble carbonates; its sodium derivative is somewhat sparingly soluble in cold water.

Methanedisulphonylbis-p-phenylenediamine,



was prepared by reducing the preceding compound with iron filings and 4 per cent. acetic acid. The reduction was completed after two hours' heating, and the mixture, rendered alkaline with sodium carbonate, was rapidly filtered. The base, which had passed into the filtrate in the form of its sodium derivative, was precipitated with dilute acetic acid, and crystallised from ethyl acetate, when it separated in small, colourless needles, melting at 227°.

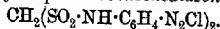
0.1505 gave 21.0 c.c. N_2 at 26° and 771 mm. $\text{N}=15.72$.

0.2036 „ 0.2691 BaSO_4 . $\text{S}=18.15$.

$\text{C}_{13}\text{H}_{10}\text{O}_4\text{N}_4\text{S}_2$ requires $\text{N}=15.73$; $\text{S}=17.97$ per cent.

Methanedisulphonylbis-p-phenylenediamine is an amphoteric substance, exhibiting in a remarkable degree the dual properties of base and acid. As a base, it forms a dihydrochloride soluble in water, and dissolving more sparingly in alcohol. As an acid, it decomposes calcium carbonate and other insoluble carbonates, and forms soluble sodium and even ammonium derivatives.

Methanedisulphonylbis-p-aminobenzenediazonium chloride,



—The foregoing base was suspended in alcohol, concentrated hydrochloric acid added, and the resulting solution rapidly filtered. Amyl nitrite was then added, when the diazonium chloride rapidly separated as a light grey, crystalline precipitate, insoluble in alcohol:

0.1114 gave 17.6 c.c. N_2 at 22° and 769 mm. $\text{N}=18.10$.

0.2090 „ 0.1276 AgCl . $\text{Cl}=15.10$.

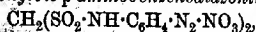
$\text{C}_{13}\text{H}_{10}\text{O}_4\text{N}_6\text{Cl}_2\text{S}_2$ requires $\text{N}=18.60$; $\text{Cl}=15.74$ per cent.

When prepared in the dark, the diazonium chloride is almost colourless, but when exposed to light in contact with its mother

liquor, the salt frequently assumes a reddish-brown colour, and becomes almost insoluble in water.

The corresponding diazonium sulphate was produced by diazotising the foregoing diamine in dilute sulphuric acid, and, being less soluble than the diazonium chloride, it was precipitated by alcohol from its aqueous solution. These salts, when dissolved in water, have an acid reaction.

Methanedisulphonylbis-p-aminobenzenediazonium nitrate,



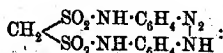
and the following substance were obtained in unsuccessful attempts to prepare the bisdiazoimide. The nitrate was formed by adding silver nitrate to an aqueous solution of the foregoing diazonium chloride, and concentrating the filtrate from the silver chloride over potassium hydroxide under 5 mm. pressure. It separated in pale yellow needles, which, when dry, were somewhat sparingly soluble in cold water, and decomposed violently at $156-160^\circ$:

0.398 gave 17.7 c.c. N_2 at 22° and 766 mm. $\text{N}=22.51$.

0.268 " 0.1580 CO_2 and 0.0365 H_2O . $\text{C}=31.50$; $\text{H}=2.96$.

$\text{C}_{13}\text{H}_{12}\text{O}_6\text{N}_8\text{S}_2$ requires $\text{C}=30.95$; $\text{H}=2.38$; $\text{N}=22.22$ per cent.

A carefully purified portion of methanedisulphonylbis-p-phenylenediamine was dissolved in glacial acetic acid, and diazotised with ethyl nitrite. The filtered solution, when gradually diluted with alcohol and ether, deposited a pale yellow, unstable substance, which, when rapidly collected and dried, gave analytical data corresponding with the diazoamine:



0.1324 gave 0.1722 CO_2 and 0.0452 H_2O . $\text{C}=41.41$; $\text{H}=4.43$.

0.1324 " 22.0 c.c. N_2 at 17° and 772 mm. $\text{N}=19.60$.

$\text{C}_{13}\text{H}_{12}\text{O}_2\text{N}_4\text{S}_2$ requires $\text{C}=42.50$; $\text{H}=3.54$; $\text{N}=19.07$ per cent.

Another portion of the base was dissolved in glacial acetic acid, diazotised with ethyl nitrite, and the solution evaporated to dryness at the ordinary temperature in a vacuum desiccator. The residue, a dark red substance resembling shellac, contained no combined acetic acid, and only 15.38 per cent. of nitrogen, showing that a portion of the diazo-nitrogen had been eliminated during evaporation. Its composition approximated to that of a diazo-oxide or azo-phenol produced by internal condensation.

The colourless aqueous solutions of the bisdiazonium salts, when treated with excess of sodium acetate, assumed an intense yellow colour, indicating the formation of the bisdiazoimide, but the substance was not precipitated. After many fruitless attempts to isolate the bisdiazoimide, it was found possible to precipitate it

either by adding the solid bisdiazonium chloride to concentrated aqueous sodium acetate or by introducing crystals of the latter salt into strong aqueous solutions of the bisdiazonium chloride. The latter procedure is preferable, because by the former the product passes through a viscid phase which is obviated by the second method of mixing. The bisdiazoinide separates as an orange yellow, microcrystalline mass, which, when once segregated, is remarkably insoluble in cold water, and can accordingly be thoroughly washed without serious loss, first with water, and then successively with ether and light petroleum:

0.1042 gave 0.1576 CO_2 and 0.0368 H_2O . $\text{C}=41.26$; $\text{H}=3.87$.

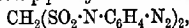
0.1272 " 0.1926 CO_2 " 0.0414 H_2O . $\text{C}=41.29$; $\text{H}=3.61$.

0.1123 " 21.9 c.c. N_2 at 19.5° and 761 mm. $\text{N}=22.43$.

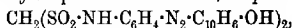
0.1712 " 0.2138 BaSO_4 . $\text{S}=17.15$.

* $\text{C}_{13}\text{H}_{10}\text{O}_4\text{N}_6\text{S}_2$ requires $\text{C}=41.26$; $\text{H}=2.64$; $\text{N}=22.22$;
 $\text{S}=16.93$ per cent.

Methanedisulphonylbis-p-phenylenediazoimide,



decomposes violently at 120° , and darkens rapidly on exposure to light. When triturated with β -naphthol in the presence of pyridine, it combined additively with the former, giving rise to *methanedisulphonylbis-p-aminobenzeneazo- β -naphthol*,



which was also produced in the form of its sparingly soluble dark red alkali derivative on adding the bisdiazonium chloride to alkaline β -naphthol. The free azo- β -naphthol is a red powder, varying considerably in tint, and only sparingly soluble in the ordinary organic media; it melts at 272° .

0.1304 gave 14.4 c.c. N_2 at 15° and 752 mm. $\text{N}=12.80$.

$\text{C}_{13}\text{H}_{20}\text{O}_6\text{N}_6\text{S}_2$ requires $\text{N}=12.61$ per cent.

IV.—*Methanesulphonyl-p-phenylenediazoimide*.

The methanesulphonyl chloride employed in the following experiments was either purchased or prepared from methyl sulphate, this ester being converted into methyl thiocyanate by means of aqueous potassium thiocyanate. Methanesulphonic acid was then produced by oxidising methyl thiocyanate with nitric acid, and freed from water as completely as possible by repeated evaporation. Treatment with phosphorus pentachloride led to the formation of a mixture of phosphoryl chloride and methanesulphonyl chloride, which was fractionated under the ordinary and also under reduced pressure. All the specimens of methanesulphonyl chloride employed contained appreciable amounts of phosphorus compounds, which,

fortunately, did not interfere seriously with the following condensation.

Methanesulphonyl-p-nitroaniline, $\text{CH}_3\cdot\text{SO}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$.

Ten grams of methanesulphonyl chloride were added to a warm toluene solution of *p*-nitroaniline (10.5 grams) and triethylamine (10 grams); a heavy, oily layer separated, and rings of triethylamine hydrochloride were projected from the flask. After boiling for fifteen minutes, the solvent was evaporated off, and the residue extracted with excess of aqueous sodium carbonate until only a slight amount of tar remained undissolved. The solution was thoroughly cooled, and the crystallised *p*-nitroaniline separated; the filtrate, acidified with hydrochloric acid gave an almost colourless precipitate of methanesulphonyl-*p*-nitroaniline, the yield being about 9 to 10 grams.

Very little condensation occurs in the absence of triethylamine, and in this respect methanesulphonyl chloride differs considerably from methionyl chloride, which reacts energetically with *p*-nitroaniline, even in the absence of any condensing agent.

Methanesulphonyl-*p*-nitroaniline crystallises readily from dilute alcohol in pale yellow needles or transparent, amber-coloured prisms; it melts at 186° :

0.1212 gave 13.9 c.c. N_2 at 20° and 756 mm. $\text{N} = 13.06$.

$\text{C}_7\text{H}_6\text{O}_4\text{N}_2\text{S}$ requires $\text{N} = 12.96$ per cent.

This nitro-compound dissolves readily in aqueous sodium carbonate or ammonia, and is slightly soluble in water; it is not reprecipitated from its alkaline solutions by acetic acid, but only by mineral acids.

Methanesulphonyl-p-phenylenediamine, $\text{CH}_3\cdot\text{SO}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$.

The foregoing nitro-compound could not be reduced satisfactorily by iron and dilute acetic acid, zinc and ammonia, aluminium amalgam, stannous chloride, or ammonium sulphide. The best result was obtained by dissolving 2 grams of nitro-compound in 20 c.c. of 50 per cent. alcohol, containing 0.5 gram of ammonium chloride. On adding excess of zinc dust to the warm solution, reduction occurred, and was completed by boiling for a short time. The alcoholic filtrate was rapidly evaporated to dryness, and the residue extracted with benzene. When crystallised from this solvent, the base separated in colourless needles, melting at 122° :

0.1327 gave 18.1 c.c. N_2 at 20° and 772 mm. $\text{N} = 15.86$.

0.1588 „ 0.2036 BaSO_4 . $\text{S} = 17.60$.

$\text{C}_7\text{H}_{10}\text{O}_2\text{N}_2\text{S}$ requires $\text{N} = 15.05$; $\text{S} = 17.20$ per cent.

The hydrochloride of methanesulphonyl-*p*-phenylenediamine, which is readily soluble in water or alcohol, separates in colourless leaflets, melting at 223°:

0.1192 gave 12.7 c.c. N₂ at 21.5° and 761 mm. N = 12.11.

C₇H₁₀O₂N₂S.HCl requires N = 12.53 per cent.

The sulphate is somewhat less soluble in water, and is precipitated by alcohol from its aqueous solution. The diazonium chloride separated in colourless plates on adding successively ethyl nitrite and dry ether to an alcoholic solution of the hydrochloride; it rapidly becomes brown and viscid on exposure to the atmosphere. The diazonium sulphate was more stable than the diazonium chloride, and separated in colourless crystals on adding ethyl nitrite and ether successively to a solution of the sulphate in glacial acetic acid.

These diazonium salts, when added to strong aqueous solutions of sodium acetate, gave either a resinous product or an intensely yellow solution, the result depending on the concentration of the sodium acetate. Only in two isolated cases was a yellow, crystalline product obtained in this way. This compound decomposed violently on gently warming, whereas the resinous product burnt quietly. The former of these substances was evidently the diazoimide, as was proved by coupling it with *β*-naphthol.

The diazoimide was obtained in the solid condition by mixing cold aqueous solutions of methanesulphonyl-*p*-phenylenediamine hydrochloride and sodium nitrite, taking these salts in accurately weighed molecular proportions. The solution was rapidly filtered four or five times, and when of a clear yellow colour was evaporated at the ordinary temperature in a vacuum desiccator over phosphoric oxide and potassium hydroxide. An orange-yellow residue was obtained, consisting of the diazoimide (decomposition point 150°) and sodium chloride in approximately molecular proportions. The mixture was ground up thoroughly, and the sodium chloride estimated as sodium sulphate after heating with pure concentrated sulphuric acid. After making allowance for the proportion of sodium chloride present, the following results were obtained:

0.1765 gave 0.2668 CO₂ and 0.0646 H₂O. C = 41.23; H = 4.06.

0.1353 „ 25.5 c.c. N₂ at 20° and 772 mm. N = 21.90.

C₇H₁₀O₂N₂S requires C = 42.64; H = 3.65; N = 21.31 per cent.

The diazotisation was now repeated, using silver nitrite instead of sodium nitrite, the dry salt being thoroughly triturated with the aqueous solution of methanesulphonyl-*p*-phenylenediamine hydrochloride. After filtering off the silver chloride, the clear yellow solution contained only the methanesulphonyl-*p*-phenylenediazoimide; the substance appeared, however, to be less stable than

in the presence of sodium chloride, and showed signs of losing some of its diazo-nitrogen. The final residue was shown to contain diazomide by coupling with β -naphthol in pyridine solution. A bright red azo- β -naphthol was produced, which melted at $244-245^\circ$, and was identical with methanesulphonyl-*p*-aminobenzene-*l*-naphthol prepared by coupling methanesulphonyl-*p*-aminobenzene-diazonium chloride with alkaline β -naphthol. In the latter preparation the azo- β -naphthol was produced in the form of its soluble alkali derivative, and was precipitated by dilute acetic acid. The free azo- β -naphthol was almost insoluble in alcohol, but crystallised readily from glacial acetic acid in red, glossy, filamentous needles; it melted at $244-246^\circ$, and dissolved in concentrated sulphuric acid to a deep red solution:

0.1147 g. gave 12.3 c.c. N_2 at 19° and 758 mm. $N = 12.30$

$C_{17}H_{15}O_3N_3S$ requires $N = 12.31$ per cent.

We desire to express our thanks to the Government Grant Committee of the Royal Society and the Research Fund Committee of the Chemical Society for grants which have partly defrayed the expenses of this investigation.

ROYAL COLLEGE OF SCIENCE, LONDON.
SOUTH KENSINGTON, S.W.

VII.—The Action of Hydrogen Dioxide on Thiocarbamides.

By EDWARD DE BARRY BARNETT.

THE action of hydrogen dioxide on thiocarbamide in oxalic acid solution was investigated by Storch (*Monatsh.*, 1890, **11**, 452), who obtained a salt of the disulphide, $NH_2C(NH_2) \cdot S \cdot S \cdot C(NH_2)NH_2$, but was unable to isolate the free base. Storch also obtained salts of this disulphide by oxidising thiocarbamide with nitric acid and other acid oxidising agents. Evidently in this case the thiocarbamide reacts in the pseudo-form. It occurred to the author to investigate the action of hydrogen dioxide on thiocarbamide in neutral or alkaline solution, as it seemed possible that in these circumstances it might react as a symmetrical diamide.

Oxidation of Thiocarbamide.

Fifteen grams of finely-powdered thiocarbamide were slowly added during an hour to 230 c.c. of 6 per cent. aqueous hydrogen

dioxide, the whole being cooled by surrounding with ice. The thiocarbamide dissolved, and after an hour the oxidation product crystallised in colourless needles. These were extracted with boiling alcohol to remove any unchanged thiocarbamide, and were dried in a vacuum over concentrated sulphuric acid. The yield was 9 grams:

0.3400 gave 0.1387 CO_2 and 0.1103 H_2O . $\text{C}=11.13$; $\text{H}=3.62$.
 0.5125 „ 0.2077 CO_2 „ 0.1850 H_2O . $\text{C}=11.05$; $\text{H}=3.82$.
 0.1465 „ 0.3225 BaSO_4 . $\text{S}=30.17$.
 0.2077 „ 45.4 c.c. N_2 (moist) at 12° and 762 mm. $\text{N}=26.2$.
 0.0736, in 20.10 water, gave $\Delta t = -0.072^\circ$. $\text{M.W.}=96$.
 $\text{CH}_4\text{O}_2\text{N}_2\text{S}$ requires $\text{C}=11.11$; $\text{H}=3.70$; $\text{S}=29.63$;
 $\text{N}=25.9$ per cent. $\text{M.W.}=108$.

From the analytical results, it is clear that Storch's disulphide is not formed under these conditions, and the molecular weight determination shows that condensation does not take place, but that each molecule of thiocarbamide takes up two atoms of oxygen. The compound has faintly acidic properties, and it does not reduce metallic salts, as would be probable if it had the structure $\text{OH}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{OH}$. Further, the ease with which it evolves sulphur dioxide on heating points to the oxygen being in direct union with the sulphur. It was also found that carbamide does not yield a similar compound.

It would appear, therefore, that its constitution is to be represented as $\text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{SO}_2\text{H}$, and, in order to confirm this, attempts were made to obtain a similar compound from thio-benzamide and thioacetamide, but these were not successful, a mixture of the amide and the unchanged thioamide being the invariable result.

Aminoiminomethanesulphinic acid melts and decomposes at 144° . It is fairly soluble in cold water, to which it imparts a faintly acid reaction, but is insoluble in organic solvents. It decomposes slowly at 100° and rapidly at 110° , sulphur dioxide being evolved. It is rapidly decomposed by boiling water, and from the solution thus obtained chloroplatinic acid precipitates an orange-red salt. This is probably formamidine platinichloride, but it has not been possible to obtain it in sufficient quantity for analysis. Aminoiminomethanesulphinic acid instantly reduces acid permanganate in the cold, and quantitative experiments showed that, in doing so it takes up one atom of oxygen. Attempts to isolate this oxidation product failed. On treatment with excess of permanganate, hydrogen cyanide is evolved. It was not found possible to prepare an acetyl derivative by treatment with acetyl chloride.

The investigation was extended to some of the derivatives of thiocarbamide in the hope of obtaining similar compounds which would give more definite decomposition products.

Preparation of Allylthiocarbamide.

Finely powdered allylthiocarbamide were gradually added during an hour to 110 c.c. of a 6 per cent. aqueous solution of hydrogen dioxide at 0° . The clear solution was evaporated almost to dryness in a vacuum over concentrated sulphuric acid, and the oil residue extracted with warm alcohol. The filtered solution was evaporated in a vacuum at the ordinary temperature, and the resulting colourless crystals were dried over concentrated sulphuric acid.

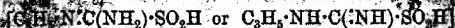
0.2442 g. gave 0.2626 CO_2 and 0.1206 H_2O . $\text{C}=29.24$; $\text{H}=5.32$.

0.2615 " " 0.2782 CO_2 " 0.1253 H_2O . $\text{C}=29.01$; $\text{H}=5.32$.

0.2558 " " 0.3556 BaSO_4 . $\text{S}=19.09$.

$\text{C}_3\text{H}_5\text{O.N.S.H.O}$ requires $\text{C}=28.92$; $\text{H}=6.02$; $\text{S}=19.27$ per cent.

This is the derivative,



tends to form a viscous oil, which only crystallises with the greatest difficulty, and hence was not obtained in a state of purity. It melts and decomposes at $165-170^{\circ}$.

Attempts were also made to prepare the substance in the pure condition by oxidising allylthiocarbamide in acetone solution with the calculated amount of aqueous 30 per cent. hydrogen dioxide. On evaporating the acetone in a vacuum, an oil was obtained, which did not crystallise after remaining under anhydrous ether for six days.

All attempts to obtain a pure product by oxidising phenylthiocarbamide, either in aqueous or in acetone solution, with hydrogen dioxide yielded a viscous oil which did not crystallise.

The ease with which the oxidation of thiocarbamides takes place seems to depend on the number of substituents present. Thus, with thiocarbamide itself, the action of hydrogen dioxide is violent, and must be carried out at a low temperature; with allylthiocarbamide and phenylthiocarbamide, the reaction is much less violent; and hydrogen dioxide has no action on thiocarbamide. This is probably to be attributed to the influence of the substituents in hindering the formation of the pseudo-form

VIII.—The Influence of Non-electrolytes on the Solubility of Carbon Dioxide in Water

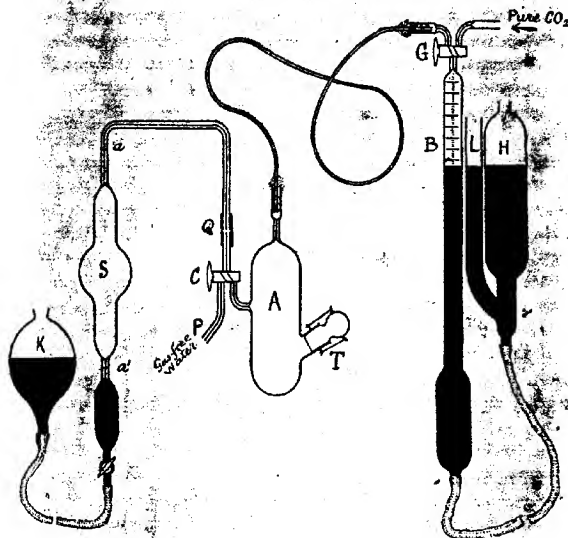
By FRANCIS LAWRY USHER.

THE object of the investigation to be described in this paper was to place upon record a larger number of accurate measurements of the solubility of a gas in solutions of non-electrolytes than has hitherto been available. Although there is a considerable mass of experimental data relating to the solubility of gases in salt solutions, the non-electrolytes examined have been confined to some sugars, chloral hydrate, carbamide, and a few slightly dissociated organic acids (Roth, *Zeitsch. physikal. Chem.*, 1897, 24, 114; Braun, *ibid.*, 1900, 33, 721; Knopp, *ibid.*, 1904, 48, 97; Christoff, *ibid.*, 1905, 53, 321; Hüfner, *ibid.*, 1906, 57, 611; Steiner, *Wied. Annalen*, 1894, 52, 275). The experiments recorded here were all carried out at 20°, and, except in the case of sucrose, at only one concentration, namely, semi-normal. The gas used was carbon dioxide, chosen because its comparatively large absorption-coefficient permitted greater accuracy in the determinations, whilst at the same time its slight deviation from Henry's law is not sufficient to preclude its use as an indifferent gas. The substances studied were sucrose, dextrose, mannitol, glycine, pyrogallol, quinol, catechol, resorcinol, carbamide, thiocarbamide, urethane, acetamide, antipyrine, acetic acid, and *n*-propyl alcohol.

EXPERIMENTAL

Except in the case of the two liquid substances examined, namely, acetic acid and *n*-propyl alcohol, the solutions were of exactly semi-normal strength, and were prepared in the absorption vessel itself. The apparatus was designed with this end in view, and a description of it will now be given. The carbon dioxide was prepared in an ordinary Kipp's apparatus, from marble which had been boiled for some time in distilled water in order to remove adhering and occluded air, and concentrated hydrochloric acid. The gas was found to contain less than 0.03 per cent. of foreign gas. The outlet tube from the Kipp's apparatus was connected through a tap with a large U-tube filled with marble chips, which served to prevent any acid spray from being carried over with the carbon dioxide. The gas was next led through a wash-bottle containing concentrated sulphuric acid, and finally through a phosphoric oxide tube. Wherever practicable, connexions between glass portions of the apparatus were made by sealing the glass together with a

mouth-blowpipe; in fact, the number of taps and rubber connexions were kept as small as possible, and the latter, when it was necessary to use them, consisted of short pieces of pressure tubing of small bore, inside of which the glass ends were brought together. The tap of the Kipp's apparatus was left permanently open, so that the internal gas pressure was always in excess of the atmospheric, and no air could leak into the apparatus. The measuring burette (B) was of 100 c.c. capacity. Of this, 50 c.c. were contained in the narrow upper part, which was graduated in tenths of a c.c., and was calibrated by weighing out mercury, whilst the



remaining 50 c.c. were contained in a bulb blown below this graduated portion. The burette was connected by rubber tubing with a mercury reservoir H, carrying a levelling tube L of the same diameter as the graduated part of the burette, and was provided at the top with a three-way tap G, by means of which it could be connected either with the carbon dioxide supply or with the absorption vessel. The absorption vessel A was of about 220 c.c. capacity, and was provided near the bottom with a tubulure T, about 14 mm. wide, carrying two small glass hooks, and which could be closed by a ground glass stopper carrying a second pair

of books, by means of which it could be held firmly in position with two elastic bands. *The solid substance was introduced through this tubulure. On the opposite side, and at the top, was a short capillary tube carrying a three-way tap, arranged that either the absorption vessel could be connected with vessel S, delivering a known volume of gas-free water; or it could be connected, independently of the absorption vessel, with the store of gas-free water employed.

A flexible copper capillary, 2 metres long and of 1 mm. bore, was used to connect the absorption vessel with the first store, and was cemented into the glass tubing with marine glue. The joints being subsequently enclosed in plaster-of-Paris blocks to prevent them from becoming loose when the absorption vessel was shaken. A thermostat was employed for all the experiments, and were carried out at $20^{\circ} \pm 0.02^{\circ}$. When the room-temperature was above 20° , a cooling coil was introduced into the thermostat, the method of carrying out a determination is as follows:

In the first place, a semi-normal solution of the substance to be examined was prepared, and its specific gravity at 20° was determined, and from this was calculated the weight of substance which would give a semi-normal solution when dissolved in 100 gms. of water, this being the amount of water used in every experiment. The exact quantity of the substance was then weighed into the absorption vessel through the tubulure, after which the capillary was inserted and fastened in position. The absorption vessel was now connected through the three-way tap with a Töpler pump and completely exhausted. After closing the tap, it was filled with pure dry carbon dioxide by alternately filling the burette from the supply and allowing the gas in the burette to pass into the absorption vessel, by suitably turning the three-way tap. The absorption vessel was now placed in the thermostat and there until the temperature of the contained gas was constant at 20° , and it was arranged that when it was full of gas at 20° under the atmospheric pressure, the level of the mercury should be at the top of the burette. The burette reading was then observed, and the room-temperature and barometric height noted. Pure gas-free water had now to be introduced. Ordinary distilled water was used, and was previously boiled out in a vacuum in a round-bottomed flask provided with a rubber stopper carrying two glass tubes, one short, the other passing to the bottom of the flask. As soon as all air had been completely removed, the flask was closed, cooled to a little below 20° , and the longer tube was then connected with the branch P of the three-way tap C, and so with the vessel S, which was filled with mercury, and of which the volume between

two marks on the capillary stem at a and a' was accurately known: this was 117.0°C . at 20° . By suitable manipulation all air was removed from the capillary tubing, and the tap C was now turned and the vessel filled with gas-free water to the lower mark a' . C was then turned in the other direction, and by raising the reservoir H and lowering the reservoir H , the exact quantity of water between a and a' was driven into the absorption vessel, which was then closed, and the absorption vessel disconnected at P and placed in the thermostat. It was then shaken vigorously until all the solid was dissolved, and the resulting solution saturated with carbon dioxide at 20° under the atmospheric pressure. When the burette reading was constant, the barometer height and room temperature were again noted, and the determination was now finished. Care was taken that no gas or liquid passed from the absorption vessel to the burette; evidently the gas in the burette was always dry, whilst that in the absorption vessel was only dry at the commencement of the experiment. For the purposes of calculation the volume, and hence the density, of the solutions used, had to be known. The values of some of these were taken from papers by Schröder (*Ber.*, 1879, 12, 161, 1880, 13, 1070), and some were redetermined.

The absorption-coefficients for the liquids, acetic acid and n -propyl alcohol, were determined by Ostwald's method, in an absorption vessel containing 246.3 c.c. Since the volume of gas absorbed in the case of these liquids was much greater than the capacity of the burette, the latter had to be refilled several times. Although the error of reading was repeated as often as the burette was filled, the volume of gas dealt with was proportionately larger, and the probable error in the final result therefore remained the same as for the other solutions, for which a single filling of the burette sufficed.

Two determinations were carried out with every solution examined, and four in the case of water. The maximum difference between the results of two such experiments was 1 in 1000, whilst most agreed to within 1 or 2 in 1000.

Calculation of Results

The absorption-coefficients (α) given represent the volume of carbon dioxide, reduced to 0° and 760 mm., which is dissolved by 1 c.c. of liquid at 20° when the partial pressure of the carbon dioxide is 760 mm.

(i) Calculation of absorption-coefficient for solution of solids:

Let V = volume of absorption vessel, W = weight of copper capillary.

- Let y = volume from beginning of copper capillary to mark "0" on burette.
 „ b_1 and b_2 = initial and final burette readings.
 „ A = volume of solution.
 „ a = volume of solid substance.
 „ P = barometric height, corrected to 0°.
 „ p = vapour pressure of solution at 20°.
 „ t = room-temperature.

The corrected initial volume of gas in the apparatus

$$\frac{P}{760} \left\{ (x-a) \cdot \frac{273}{293} + (b_1+y) \cdot \frac{273}{273+t} \right\},$$

and the corrected final volume will be:

$$\left\{ \frac{P-p}{760} (x-A) \cdot \frac{273}{293} + \frac{P}{760} (b_2+y) \cdot \frac{273}{273+t} \right\}$$

hence the volume dissolved by A c.c. of the solution

$$= \frac{P}{760} \cdot \frac{273}{273+t} (b_1-b_2) + \frac{273}{293} \left\{ \frac{P}{760} (x-a) - \frac{P-p}{760} (x-A) \right\} \text{ c.c.}$$

and

$$a = \frac{\frac{P}{P-p} \cdot \frac{273}{273+t} (b_1-b_2) + \frac{273}{293} \left\{ \frac{P}{P-p} (x-a) - (x-A) \right\}}{A}$$

If the room-temperature is itself 20°, the expression simplifies to:

$$a = \frac{\frac{273}{293} \left\{ \frac{P}{P-p} (x-a+b_1-b_2) - (x-A) \right\}}{A}$$

(ii) When water is used instead of a solution of a solid, if W is the volume of water taken:

$$a = \frac{\frac{P}{P-p} \left\{ \frac{273}{273+t} (b_1-b_2) + \frac{273}{293} x \right\} - \frac{273}{293} (x+W)}{W}$$

or

$$a = \frac{\frac{273}{293} \left\{ \frac{P}{P-p} (b_1-b_2+x) - (x+W) \right\}}{W}$$

if the room-temperature is 20°.

(iii) In the case of the solutions of liquids examined, the absorption-coefficient, measured in the Ostwald vessel, is equal to:

$$\frac{\frac{P}{P-p} \cdot \frac{273}{273+t} \left\{ \Sigma(b) - \Sigma(b') \right\} - \frac{273}{293} W}{A}$$

where b and b' are the burette readings before and after intro-

ducing the gas into the absorption vessel, and W is the volume of solution run out from the absorption vessel.

Nature and Magnitude of Errors.

In all the experiments, an accuracy of 1 in 1000 was aimed at, and the values of α given may be taken as correct to 1 in 500. Since the measured volume difference between the first and last readings was always about 100 c.c., an error of 0.1 c.c. involves an error of 1 in 1000 in the value of α . By far the most important sources of error were (1) inexact levelling when reading the volume of gas in the burette, and (2) variations in the temperature of the thermostat.

There was no difficulty in reading the burette with a maximum error of 0.05 c.c., but the exact adjustment of the levelling tube was not so easy. In the initial reading, when the volume of gas in the apparatus is about 225 c.c., an error of 1 mm. in the levelling involves an error of about 0.33 c.c. In the final reading, when the volume of gas is only half as great, a similar error in levelling involves an error of 0.17 c.c. The actual uncertainty of levelling was probably about a quarter of a millimetre, and if the errors in the two readings were additive, this involves an error of 1.2 in 1000 in the value of α . Thus the probable error introduced by this inaccuracy is 0.6 in 1000.

Variations in temperature affect the results in two ways. Thus, if the temperature of the thermostat is not exactly 20° , not only is the volume of gas soluble in the liquid changed by expansion or contraction, but the absorption-coefficient is also directly influenced. Supposing that at the initial reading the true temperature in the thermostat is $(20 - \theta)^\circ$, and at the final reading it is $(20 + \theta)^\circ$, it can be calculated that the difference between the true and the apparent volume of gas absorbed is:

$$\beta + \frac{27300\theta}{293^2 + 293\theta} + \frac{60060\theta}{293^2 - \theta^2} \text{ c.c.},$$

where β is the difference between the volume of gas soluble in the liquid at 20° and the volume soluble at $(20 + \theta)^\circ$. This expression, after neglecting θ and θ^2 in the denominator, and evaluation of β from the temperature-coefficient of solubility of carbon dioxide in water, is equal to about 4\theta c.c. Now the maximum variation (2θ) in the temperature of the thermostat was 0.04° , and the maximum error from this cause is therefore 0.08 c.c., that is, about 0.8 in 1000.

Compared with the above, the other errors are unimportant. The barometer was read with an accuracy of 0.1 mm., and the height of the mercury column was corrected for expansion from

0° to the room-temperature. The time interval between the initial and final readings was usually about half an hour, and no sensible error was introduced through employing the mean temperature for barometer readings, since these never differed by more than 0.5 mm., and could not as a rule be detected. Similarly, the room-temperature was always sufficiently constant during the experiment to preclude the introduction of any appreciable error through employing the mean temperature for the calculations. There is no doubt that the gas in the absorption vessel was completely saturated with water vapour at the second reading, owing to the vigorous shaking which always took place, or that the gas in the burette was dry, since the burette tap was always closed while the absorption vessel was being shaken, and gas was never allowed to pass from the latter into the burette. As already stated, two determinations were made in every case, in which the average difference is 1.7 in 1000, and consequently the probable accuracy of the results is about 1 in 1000.

Results.

Absorption-coefficient in Water.—Four determinations were made, and the values found were (i) 0.8775; (ii) 0.8766; (iii) 0.8755; (iv) 0.8766; mean, 0.877.

This value is in good agreement with that given by Böhr (*Wied. Annalen*, 1899, 69, 503), namely, $\alpha_{20} = 0.878$.

Table I gives the absorption-coefficients (α') in the solutions of sucrose examined, and the specific gravities of the solutions.

TABLE I.

Concentration.	α' .	Mean α' .	Sp. Gr.
N/8	0.8465 0.8449	0.846	1.015
N/4	0.8161 0.8140	0.815	1.032
N/2	0.7554 0.7563	0.756	1.052
N	0.6491 0.6496	0.649	1.125

In table II are given the absorption-coefficients in semi-normal solutions of the other substances examined, and, for purposes of reference, the specific gravities of the solutions at 20° and the specific gravities of the solid substances at the same temperature.

TABLE II.

	n_D^{20}	Mean n_D^{20}	Sp. gr. N/2-solution.	Sp. gr. solid.
Dioxane	0.7914	0.792	1.0328	1.56 *
	0.7928			
Methyl acetate	0.7822	0.782	1.03031	1.46 *
	0.7811			
Diethyl ether	0.8425	0.843	1.01413	1.81 *
	0.8443			
Triethyl ether	0.8529	0.858	1.01718	1.45
	0.8545			
Orange oil	0.8553	0.887	1.00946	1.33
	0.8375			
Essential oil	0.9002	0.901	1.00958	
	0.9024			
Essential oil	0.8676	0.868	1.0107	
	0.8692			
Urethane	0.8690	0.889	1.0037	0.9
	0.8682			
Carbamide	0.8634	0.864	1.00715	
	0.8640			
Thiourea	0.8604	0.859	1.00917	
	0.8581			
Acetamide	0.8584	0.859	1.01339	
	0.8600			
Acetamide	0.8790	0.879	1.0005	1.5
	0.8785			
Acetic acid	—	0.883	1.0026	
n-Propyl alcohol	—	0.889	0.9939	

* Redetermined.

Discussion of Results.

Since any theoretical deductions from the results must depend on the way in which the latter are expressed, it is first of all desirable to consider briefly the methods which are usually employed for this purpose. In order to compare together a number of different substances with respect to their influence on the solubility of a third substance, it is, of course, only permissible to employ solutions of the same molecular concentration. Here the usual difficulty arises with regard to the calculation of molecular concentration (compare Abegg, *Zeitsch. physikal. Chem.*, 1894, 16, 248). The semi-normal solutions used in this investigation all contained half a gram-molecule in a litre of the solution, and this concentration is in many cases considerably different from that of a solution containing the same weight of substance in 1000 grams of water. Except in the case of sucrose, no experiments with several different concentrations were carried out, but the figures for this substance certainly suggest that the volume-normal is more convenient for our present purpose than the weight-normal method of calculation, and also that solutions of semi-normal

strength are still sufficiently dilute to permit inferences which may be applied without serious error to very-dilute solutions.

In table III are given values for the molecular depression of solubility calculated according to the volume-normal and weight-normal methods for solutions of sucrose. α and α' are the absorption-coefficients of carbon dioxide in pure water and the solution respectively, N is the number of gram-molecules of sucrose in 1 litre of solution, and N' the number in 1000 grams of water.

TABLE III.

N .	$\alpha - \alpha'/N$.	$\alpha - \alpha'/N'$.
0.125	0.248	0.241
0.25	0.248	0.234
0.5	0.242	0.216
1.0	0.228	0.180

It will be seen from these figures that the molecular depression, calculated by the volume-normal method, is constant for solutions up to $N/4$, and is very little different for those of $N/2$ concentration; and since sucrose produces a much greater effect than any of the other substances examined, the deviations in the case of these must be still smaller. The purely empirical formula, $\alpha - \alpha'/N^{\frac{1}{2}}$, suggested by Jahn for expressing the relation between depression of solubility and concentration in the case of electrolytes, is obviously unsuitable for sucrose, and Roth (*Zeitsch. physikal. Chem.*, 1897, **24**, 114) has shown that the figures for glycerol are better represented by the linear formula. It is therefore probably safe to assume that for moderately dilute solutions of non-electrolytes the effect on the solubility of carbon dioxide, or of any indifferent slightly soluble third substance, is directly proportional to the amount of non-electrolyte present. It now remains to consider certain attempts at generalisation in the light of the experimental data recorded in this paper.

One of the most recent of such attempts is that of Philip (*Trans.*, 1907, **91**, 711), who suggests that substances which have no tendency to combine with the solvent are without influence on the solubility of an indifferent gas, whilst those which do influence the solubility do so because they remove a portion of the solvent by forming compounds with the latter. By "solubility" is here meant the amount of gas dissolved by unit mass of the pure solvent. For example, the absorption-coefficient of hydrogen in an aqueous solution of chloral hydrate is smaller than in pure water (Knopp, *Zeitsch. physikal. Chem.*, 1904, **48**, 97), but the amount dissolved

* It should be mentioned that Geffcken (*Zeitsch. physikal. Chem.*, 1904, **49**, 257) has pointed out sources of error in the experiments of Gordon, Roth, and Braun, which may invalidate the apparent support they afford to Jahn's empirical formula.

by 1000 grams of water is the same in each case. This statement is not true, however, for solutions of sucrose; and in order to bring this substance into line, it is assumed that the statement would be true if it were not that a certain fraction of the water is withdrawn by the sucrose, and the average number of water molecules attached to one molecule of sucrose is calculated in a way consistent with the theory. This method of calculation involves three assumptions: it presupposes (1) that hydrates are formed, (2) that the gas is insoluble in the dissolved substance, and (3) that it is insoluble in the hydrate.

That such assumptions as these have little foundation in fact may be inferred from the following table, which shows the volume of carbon dioxide dissolved by 1000 grams of pure water for the different semi-normal solutions examined, calculated on the assumption that the water alone is responsible for the absorption of gas observed.

TABLE IV.

Solution.	Carbon dioxide dissolved by 1000 grams of water, in c.c.	Solution.	Carbon dioxide dissolved by 1000 grams of water, in c.c.
Water	878	Catechol	808
Sucrose	797	Urethane	907
Dextrose	841	Carbamide	884
Mannitol	833	Thiocarbamide ..	885
Glycine	864	Antipyrine	935
Pyrogallol	894	Acetamide	906
Quinol	928	Acetic acid	893
Resorcinol	945	n-Propyl alcohol...	902

It is noticeable, in the first place, that in eleven out of the fifteen solutions examined a larger quantity of carbon dioxide is dissolved than can be accounted for if the water only is responsible for the absorption. This fact alone suffices to show that if we wish to express the solvent properties of these solutions in terms of the properties of their components, any conclusions depending on the assumption that the dissolved substance has no solvent power are worthless.

It is instructive also to compare, from the point of view of the hydrate theory, the behaviour of some of these substances with that of the solutions used by Jones and Getman (*Amer. Chem. J.*, 1904, 32, 308) in their cryoscopic investigations. If the "average molecular hydration" is calculated in the way described by Philip from the figures given above for sucrose, dextrose, and mannitol, we arrive at the conclusion that sucrose is hydrated to the extent of 3.6 molecules of water, dextrose 4.6 molecules, and mannitol 5.2 molecules—values which are completely at variance with those deduced by Jones and Getman from their data for the molecular

depression of the freezing point. These authors conclude that sucrose in semi-normal solution at 0° forms complexes containing about 5 molecules of water, whereas dextrose is hydrated only to a small extent, and the tendency of mannitol to form hydrates is insignificant. It is not intended here to dispute the existence of hydrates in solution, but it may be permissible to raise the question whether much is to be gained by referring abnormal depression of solubility to this cause, when by so doing it becomes necessary to make other and more improbable assumptions.

Of a different character is the generalisation deduced from thermodynamic principles, by Jahn (compare Roth, *Zeitsch. physikal. Chem.*, 1897, 24, 115). According to this, the molecular concentration of a gas remains the same when it is dissolved to saturation in a dilute solution of an indifferent non-volatile substance as when it saturates the pure solvent under the same conditions of temperature and pressure. In other words, if C_1 denotes the ratio of the number of gas-molecules to the sum of the molecules of gas and solvent, and C_2 is the ratio of gas-molecules to the sum of those of gas, solvent, and third substance, the theory requires that C_1/C_2 shall be equal to unity, provided that the following conditions are fulfilled: (i) The gas must exert no chemical action on the solvent or the solution; (ii) it must have the same molecular weight in the liquid as in the gas phase; (iii) the solution must be dilute.

In a limited number of cases, results have been obtained which are described as being in good agreement with the theory. Roth (*loc. cit.*), using nitrous oxide, found $C_1/C_2 = 1.009$ for carbamide at about semi-normal concentration, 1.013 for nitric acid, and 1.009 for oxalic acid. Braun (*loc. cit.*) found 1.032 for carbamide and 1.023 for propionic acid in the case of nitrogen; and, in the case of hydrogen, 1.015 for propionic acid. Knopp (*loc. cit.*) found for chloral hydrate, when hydrogen was used, 0.993, and when nitrous oxide was used, the ratio was 1.010 for chloral hydrate and 1.037 for propionic acid.

Here we have values of C_1/C_2 deviating by anything between 0.7 and 3.7 per cent. from the theoretical value, but in view of the fact that the actual change of solubility effected lies between the limits 1.3 and 4.5 per cent., it becomes obvious that the apparently good agreement has no significance whatever. It should be mentioned that Knopp's experiments were all carried out at 20° , whilst those of Roth and Braun were carried out at 5° , 10° , 15° , 20° , and 25° . The figures quoted above refer to the mean of the results obtained at these five temperatures, the actual value of C_1/C_2 was found to diminish with rising temperature.

In table V the values of C_1/C_2 for the substances employed in the present investigation are tabulated, and it is, interesting to compare the percentage deviations from the theory, given in the third column, with the percentage change in solubility of the gas brought about by the non-electrolytes used, given in the fourth column.

TABLE V.

Substance	C_1/C_2	Percentage deviation from $C_1/C_2=1$.	Percentage change of solubility.
N/2 Sucrose	1.101	10.1	26.0
A/2 Sucrose	1.012	1.2	3.5
N/2 Sucrose	1.024	2.4	7.1
N/2 Sucrose	1.048	4.8	13.8
N/2 Dextrose	1.056	5.6	9.7
N/2 Mannitol	1.065	6.5	10.2
N/2 Glycine	1.026	2.6	3.0
N/2 Propagol	0.9921	0.8	
N/2 Thiocarbamide	1.002	0.2	
N/2 Carbamide	1.003	0.3	
N/2 Ethane	0.9789	2.1	
N/2 Ureine	0.9494	5.1	
N/2 Ethanol	0.9762	2.4	
N/2 Ethanol	0.9554	4.5	
N/2 Resorcinol	0.9396	6.1	
N/2 Acetamide	0.9795	2.1	0.2
N/2 Acetic acid	0.9936	0.6	1.0
N/2 Propyl alcohol	0.9817	1.8	1.0

It will be seen from this table that in no less than seven instances the deviation from the theory actually exceeds the magnitude of the effect which is being studied; and, in general, the extent of the deviation increases with the amount of the effect produced. There can, however, be no doubt that the formula deduced by Jahn is applicable to the experimental data hitherto available; in other words, that the conditions for which the formula is valid are not fulfilled in the experiments. Indeed, the influence of most non-electrolytes is so small that it may reasonably be doubted whether a rigid confirmation of the theory is possible with our present method of determining gas-solubility; and in any case there is the possibility that the dissolved substance, although chemically indifferent, may itself be capable of dissolving the gas employed.

An attempt has been made by Roth (*Zeitsch. physikal. Chem.*, 1903, 43, 539) to find some common factor which will bring the deviations from Jahn's thermodynamic formula into line with deviations from van't Hoff's freezing-point law, and it was shown that a parallelism did exist in the cases of glycerol and sucrose, both of which give too large a depression of the freezing point, and too great a value for C_1/C_2 . Thiocarbamide and glycine, however, give too small depressions, whereas the values of C_1/C_2

for these substances are respectively 1.002 and 1.026 in semi-normal solution at 20°, and would, of course, be greater still at 0°.

It seems, therefore, that the effect on the solubility of a gas* produced by non-electrolytes is not capable of explanation by reference either to the formation of hydrates in solution or to deviations from the theory of osmotic pressure—conclusions which have already been expressed by Levin (*Zeitsch. physikal. Chem.*, 1906, 55, 513); but that since these effects are, as Gefken (*loc. cit.*) has shown, practically independent of the solubility of the gas and almost entirely determined by the nature of the solvent or solution, it is only possible at present to refer them to mutual interaction among the molecules. It only remains to be mentioned that the last-named author has already called attention to parallelism which exists between depression or elevation of solubility and such properties as compressibility and surface tension, and it is possible that the whole problem might be more successfully attacked from this point of view.

This research was carried out at the suggestion of Prof. Rothmund, to whom I am greatly indebted for much kindly advice and criticism, as well as for placing at my disposal the necessary apparatus and material.

INSTITUTE OF PHYSICAL CHEMISTRY,
GERMAN UNIVERSITY,
PRAGUE.

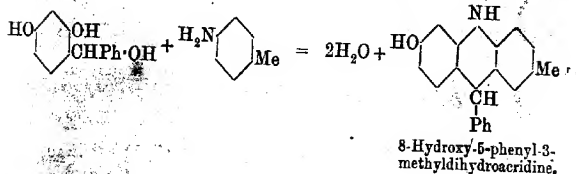
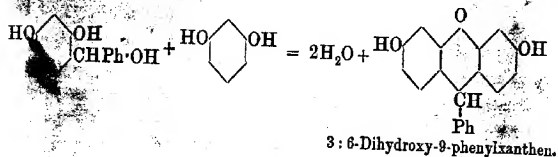
IX.—The Condensation of Benzaldehyde with Resorcinol.

By FRANK GEORGE POPE and HUBERT HOWARD.

THE reaction between benzaldehyde and resorcinol has apparently been very little studied. Michael (*Amer. Chem. J.*, 1884, 5, 338), by the addition of small quantities of hydrochloric acid to an alcoholic solution of the two reacting substances, obtained a resin to which he assigned the empirical formula $C_{26}H_{20}O_4$. This substance yielded a tetra-acetate, and also, on treatment with more acid, was converted into a crystalline isomeride. Liebermann and Lindenbaum (*Ber.*, 1904, 37, 1171), by heating an alcoholic solu-

* And also of a slightly soluble salt (compare Rothmund, *Zeitsch. physikal. Chem.*, 1909, 69, 523).

tion of the two components with concentrated sulphuric acid, obtained a compound having the composition $C_{13}H_{10}O_3$, which on acetylation yielded a triacetate. Since the above method of procedure was, to all intents and purposes, unproductive, it occurred to us that by using Manasse's method of condensation (*Ber.*, 1894, 27, 2409) the two reacting components might yield 2:4-dihydroxybenzhydrol, which would then be of considerable use in the preparation of substituted fluorones and acridines. We have succeeded in obtaining the hydrol, and have condensed it with various phenols and amines and prepared the corresponding xanthenes and dihydroacridines, as typical examples of which may be taken the reaction between the hydrol and resorcinol and the hydrol and *p*-toluidine, thus:



EXPERIMENTAL.

2:4-Dihydroxybenzhydrol, $C_6H_3(OH)_2 \cdot CH(OH) \cdot C_6H_5$.—Twenty-two grams of resorcinol were dissolved in 500 c.c. of water, containing 50 grams of sodium hydroxide, and shaken from time to time with the calculated amount of benzaldehyde (21.2 grams). The solution gradually darkened in colour, and became ultimately deep blood-red, the odour of the benzaldehyde gradually disappearing. The next day the solution was diluted with about its own volume of water, and then acidified with either dilute hydrochloric or acetic acid, when a pale brownish-white, microcrystalline precipitate of the hydrol was obtained. This was collected, well washed with water, redissolved in sodium hydroxide solution, and again precipitated and washed. It is to some extent soluble in alcohol or glacial acetic acid, and more readily so in pyridine, but cannot be recovered in a crystalline form from these solvents. For purposes of analysis, the reprecipitated hydrol was repeatedly

extracted with hot water, collected, and well washed and finally dried in a desiccator over sulphuric acid:

0.1100 gave 0.2916 CO_2 and 0.0585 H_2O . $\text{C} = 72.30$; $\text{H} = 5.91$.

0.2222 " 0.5888 CO_2 " 0.1025 H_2O . $\text{C} = 72.27$; $\text{H} = 5.13$.

$\text{C}_{13}\text{H}_{10}\text{O}_3$ requires $\text{C} = 72.22$; $\text{H} = 5.56$ per cent.

2: 4-Dihydroxybenzhydrol is a faintly yellowish-coloured substance, which darkens rather rapidly on exposure to air. It does not melt, but chars at about 200° . It is readily soluble in solutions of the alkali hydroxides, the solutions possessing a dark blood-red colour. By dissolving the hydrol in water containing the calculated amount of potassium hydroxide and evaporating the solution to dryness on the water-bath, a red dipotassium compound is obtained. On recrystallisation from water, this gave, on analysis:

0.328 gave 0.196 K_2SO_4 . $\text{K} = 26.79$.

$\text{C}_{13}\text{H}_{10}\text{O}_3\text{K}_2$ requires $\text{K} = 26.69$ per cent.

The diacetyl derivative was prepared by heating 5 grams of the hydrol with 25 grams of acetic anhydride and 1 gram of sodium acetate for three hours under reflux. The solution was filtered and poured into a mixture of 300 c.c. of water and 50 c.c. of alcohol, and the whole then warmed on the water-bath for some time to remove excess of acetic anhydride. The solid product was collected, washed, and recrystallised from dilute acetic acid, when it was obtained as a colourless solid, which decomposes when heated to about 200° :

0.1092 gave 0.2736 CO_2 and 0.048 H_2O . $\text{C} = 68.33$; $\text{H} = 4.38$.

0.1042 " 0.2604 CO_2 " 0.0466 H_2O . $\text{C} = 68.15$; $\text{H} = 4.97$.

$\text{C}_{17}\text{H}_{16}\text{O}_5$ requires $\text{C} = 68.00$; $\text{H} = 5.33$ per cent.

2: 4-Diacetoxybenzhydrol is soluble in acetone, chloroform, benzene, or acetic acid, but insoluble in light petroleum.

The benzoyl derivative was prepared by dissolving 4.32 grams of the hydrol in the calculated amount of sodium hydroxide (2 mols.) dissolved in 40 c.c. of water, and adding 5.62 grams of benzoyl chloride. The mixture was well shaken, and the pale yellow precipitate collected, washed, and crystallised from dilute acetic acid:

0.1014 gave 0.284 CO_2 and 0.0429 H_2O . $\text{C} = 76.38$; $\text{H} = 4.70$.

0.2262 " 0.6372 CO_2 " 0.096 H_2O . $\text{C} = 76.82$; $\text{H} = 4.75$.

$\text{C}_{27}\text{H}_{20}\text{O}_5$ requires $\text{C} = 76.41$; $\text{H} = 4.72$ per cent.

2: 4-Dibenzoyloxybenzhydrol is an almost colourless solid, which darkens somewhat on exposure. It is soluble in benzene, chloroform, or acetic acid, but insoluble in light petroleum. On heating, it darkens at about 170° , and melts and decomposes at about 195° .

The dimethyl ether was obtained as follows. 4.5 Grams of

potassium hydroxide were dissolved in 50 c.c. of methyl alcohol, 4 grams of the hydrol were added, along with 6 grams of methyl iodide, and the whole was heated under reflux for four hours. The solution was then diluted with water, and rendered just acid. The dark precipitate thus obtained was collected, washed, and crystallised from dilute acetic acid, from which it was obtained as a rather brownish-coloured, microcrystalline solid:

0.093 gave 0.2516 CO₂ and 0.054 H₂O. C=73.78; H=6.45.

0.109 „ 0.294 CO₂ „ 0.062 H₂O. C=73.56; H=6.32.

C₁₅H₁₆O₃ requires C=73.77; H=6.56 per cent.

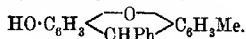
Since the above analyses would not absolutely exclude the possibility that the compound might be a monomethyl ether, C₁₄H₁₄O₃, which would require C=73.05, H=6.09 per cent., the methoxyl groups were estimated by the Zeisel method, with the following result:

0.8104 gave 0.162 AgI. OMe=26.38.

C₁₃H₁₀O(OMe)₂ requires OMe=25.41 per cent.

2: 4-Dimethoxybenzhydrol is soluble in acetone, benzene, or acetic acid. It decomposes when heated above 130°.

6-Hydroxy-9-phenyl-2-methylxanthen,



—Four grams of 2: 4-dihydroxybenzhydrol were mixed with 2 grams of *p*-cresol and 4 grams of anhydrous zinc chloride, and the mixture was heated to 170° for four hours. When cold, the product was extracted with hot water several times to remove zinc salts, and finally crystallised from alcohol. It is a red,* crystalline solid, which melts at 112°, and it is readily soluble in alcohol, but sparingly so in acetic acid:

0.111 gave 0.338 CO₂ and 0.057 H₂O. C=83.05; H=5.70.

C₂₀H₁₆O₂ requires C=83.33; H=5.56 per cent.

3: 6-Dihydroxy-9-phenylxanthen, HO·C₆H₃ $\begin{array}{c} \diagup \text{O} \diagdown \\ \text{CHPh} \end{array}$ C₆H₃·OH,

is obtained in a similar manner when 4 grams of dihydroxybenzhydrol are heated with 2 grams of resorcinol and 4 grams of anhydrous zinc chloride for four hours to 160°. It crystallises from alcohol in small red* needles, which melt at 136°, and are soluble in alcohol, pyridine, benzene, or glacial acetic acid:

0.1068 gave 0.3075 CO₂ and 0.0475 H₂O. C=78.52; H=4.94.

C₁₉H₁₄O₃ requires C=78.62; H=4.83 per cent.

* In this case the colour observed is, in all probability, due to slight oxidation with consequent formation of small quantities of the corresponding fluorone derivatives, the xanthenes being difficult to keep in a state of absolute purity.

3: 6-Dibenzoyl-9-phenylxanthen was prepared by the Schotten-Baumann method, and on recrystallisation from dilute alcohol was obtained as a rather reddish-coloured solid, melting and decomposing at 125°:

0.1082 gave 0.3148 CO₂ and 0.0446 H₂O. C=79.35; H=4.58.

C₃₃H₂₂O₂ requires C=79.52; H=4.42 per cent.

A bromo-derivative was obtained when the dihydroxyxanthen was dissolved in glacial acetic acid, and the calculated amount of bromine added gradually to the solution. A precipitate was formed at first, but dissolved on adding more of the bromine. After some time the solution was poured into water. The precipitate was collected, washed, dried, and crystallised from amyl acetate, from which it separated in small, red needles. It is soluble in amyl acetate, pyridine, chloroform, or acetic acid, but sparingly so in alcohol, the solution obtained resembling that of eosin in alcohol, and possessing a yellowish-green fluorescence:

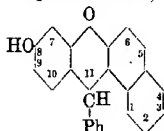
0.15 gave 0.1866 AgBr. Br=52.94.

C₁₉H₈O₃Br₄ requires Br=52.98 per cent.

C₁₉H₁₀O₃Br₄ „ Br=52.80

It is most probable that this bromo-compound is tetrabromo-3-hydroxy-9-phenylfluorone, C₁₉H₈O₃Br₄, the first action of the bromine being that of an oxidising agent, since an alcoholic alkaline solution of the bromo-compound, on treatment with zinc dust, gives a colourless solution, which rapidly oxidises with the formation of the deep red colour shown by the bromo-derivative in alcoholic alkaline solution.

8-Hydroxy-11-phenyl-β-naphthaxanthen,



—4.32 Grams of the hydrol were mixed with 2.88 grams of β-naphthol and 5 grams of anhydrous zinc chloride, and the mixture was heated to 150° for six hours. The zinc salts were extracted with water, and the residue was dissolved in dilute sodium hydroxide solution. Acetic acid was then added, and the precipitate obtained was collected and well washed with water. On recrystallisation from alcohol, the compound separated as a dark red,* crystalline powder, melting at 84°:

0.1124 gave 0.3506 CO₂ and 0.0506 H₂O. C=85.07; H=5.05.

C₂₃H₁₆O₂ requires C=85.18; H=4.94 per cent.

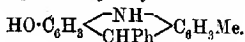
* See footnote, p. 81.

The *benzoyl* derivative (8-benzoyloxy-11-phenyl- β -naphthaxanthen) was prepared by the Schotten-Baumann method, and on recrystallisation from alcohol was obtained in small, almost colourless needles, decomposing when heated to about 103°:

0.103 g. gave 0.318 CO₂ and 0.046 H₂O. C=84.20; H=4.96.

C₃₀H₂₀O₃ requires C=84.11; H=4.67 per cent.

8-Hydroxy-5-phenyl-3-methyldihydroacridine,



—This substance was prepared by heating 8.64 grams of the hydrol with 4.28 grams of *p*-toluidine and 10 grams of anhydrous zinc chloride for four hours at 160°. The product was then boiled with water and crystallised from dilute alcohol. Owing to the obstinate retention of small traces of zinc salts, it was then found advisable to boil the product again with very dilute hydrochloric acid, filter, well wash, and again recrystallise. The product thus obtained was a light brownish-coloured * powder:

0.1002 g. gave 0.3082 CO₂ and 0.055 H₂O. C=83.88; H=6.09.

0.115 „ 5.0 c.c. N₂ (dry) at 22° and 761 mm. N=5.04.

C₂₀H₁₇ON requires C=83.62; H=5.92; N=4.88 per cent.

The *benzoyl* derivative (8-benzoyloxy-5-phenyl-3-methyldihydroacridine) was prepared by the Schotten-Baumann reaction. On crystallisation from dilute alcohol it separated in almost colourless needles, which decomposed at about 135°:

0.108 g. gave 0.3274 CO₂ and 0.0516 H₂O. C=82.67; H=5.31.

0.52 „ 17.4 c.c. N₂ (dry) at 21° and 740 mm. N=3.77.

C₂₇H₂₁O₂N requires C=82.86; H=5.26; N=3.58 per cent.

We are at present engaged on the oxidation of the xanthen and dihydroacridine derivatives, also in the condensation of the substituted benzaldehydes with phenols and amines, and hope to be able to lay the results before the Society later.

EAST LONDON COLLEGE
(UNIVERSITY OF LONDON).

* The colour here again is to be attributed to slight oxidation.

X.—The Relation between the Strengths of Acids and Bases, and the Quantitative Distribution of Affinity in the Molecule. Part II.

By BERNHARD FLÜRSCHHEIM.

In Part I (Trans., 1909, 95, 718)* it has been shown how the hitherto inexplicable influence which many substituents exercise on the dissociation constants of acids and bases can be approximately foreseen if the electropolar nature of the substituent is taken into consideration, and also the amount of chemical force required for its linking and the steric effect exercised by it on the electrolytic equilibrium. Mention was also made of the fact that all known constants of amines are in harmony with the theory, with the exception of the chloro- and bromo-anilines and *p*-aminophenol. The latter compound and *p*-anisidine will be dealt with in Part III; the present paper is concerned with the halogen-substituted anilines, and, in view of conflicting values given by different authors, also with the toluidines. Further, a graphic method has been devised by which the superposition of the three factors can be better illustrated than by the tabular arrangement previously given. Lastly, an analysis of the constitution of some derivatives of triphenylcarbinol, etc., is intended to demonstrate how these views may be applied with advantage to the elucidation of some disputed problems.

1.—The Dissociation Constants of *p*-Toluidine, *m*-Toluidine, *p*-Chloroaniline, *m*-Chloroaniline, *p*-Bromoaniline, and *m*-Bromoaniline.

The following values have been hitherto obtained:

<i>p</i> -Toluidine.....	1.56×10^{-9} (at 25°, $k_a = 1.18 \times 10^{-14}$) (Bredig, <i>Zeitsch. physikal. Chem.</i> , 1894, 13, 303); 1.13×10^{-8} (at 25°, $k_a = 1.18 \times 10^{-14}$) (Farmer and Warth, Trans., 1904, 85, 1713); 4.5×10^{-10} (at 15°) (Velej, Trans., 1906, 93, 2122); 2.2×10^{-10} (at 25°) (Denison and Steele, Trans., 1906, 89, 999, 1386).
<i>m</i> -Toluidine	5.9×10^{-10} (at 25°, $k_a = 1.18 \times 10^{-14}$) (Bredig, <i>loc. cit.</i>); 2.9×10^{-10} (at 25°, $k_a = 1.18 \times 10^{-14}$) (Farmer and Warth, <i>loc. cit.</i>); 3.9×10^{-10} (at 14°) (Velej, <i>loc. cit.</i>).
<i>p</i> -Chloroaniline...	1.49×10^{-10} (at 25°) (Farmer and Warth); 1.24×10^{-11} (at 10°) (Velej).

* In Part I, page 727, line 11 from below, the passage "the strength of linkings is more affected . . ." should read "the strength of linkings is less affected . . ." This principle has been correctly applied in the tables. Also page 728, line 3, "0.00158" should read "0.00149." Some printers' errors have been corrected in the list of "Errata."

<i>m</i> -Chloroaniline...	8.58×10^{-12} (at 10°) (Veley).
<i>p</i> -Bromoaniline ...	2.07×10^{-10} (at 18°) (Veley); 1.04×10^{-10} (at 25°) (Farmer and Warth).
<i>m</i> -Bromoaniline...	9.5×10^{-11} (at 19°) (Veley).

All these constants have been determined by hydrolysis, either by electrical conductivity (Bredig), or by an indicator (Veley), distribution (Farmer and Warth), and velocity of migration (Denison and Steele). In addition, hydrolytic values have been determined for some of these bases electrolytically by Walker (*Zeitsch. physikal. Chem.*, 1889, **4**, 319), and colorimetrically by Lellmann and Götz (*Annalen*, 1893, **274**, 139), but no constant has been calculated. According to Walker, the relative strength, beginning with the weakest, is: *m*-chloroaniline, *p*-chloroaniline; *p*-toluidine, aniline, *m*-toluidine, and, according to Lellmann and Götz: *m*-chloroaniline, *m*-bromoaniline, *p*-chloroaniline, *p*-bromoaniline; aniline, *p*-toluidine. After due allowance has been made for the effect of the differing temperatures chosen by Veley, his series would be: *m*-chloroaniline, *p*-chloroaniline, *m*-bromoaniline, *p*-bromoaniline; aniline, *m*-toluidine, *p*-toluidine. The series of Farmer and Warth is: *p*-bromoaniline, *p*-chloroaniline; *m*-toluidine, aniline, *p*-toluidine; and that of Bredig: aniline, *m*-toluidine, *p*-toluidine.

If this mass of contradictory evidence is sifted in the light of the present theory, *m*-toluidine should be stronger than aniline (compare Part I, tables). Similarly, *m*-bromoaniline should be stronger than *m*-chloroaniline, for the same reason that *m*-bromobenzoic acid is weaker than *m*-chlorobenzoic acid (compare Part I, tables). The relative strength of the meta- and para-halogen-substituted compounds is, however, theoretically not quite so simply deduced. It is well known that many substituents exercise a stronger polar influence from the para- than from the meta-position, notwithstanding the greater number of intervening atoms, which, in an open chain, reduce the polar effect of a substituent. This can only be due to a direct neutralisation of residual affinity between the para-atoms, as has been assumed in the benzene formula of Claus. The strength of this diagonal bond is, however, variable, for it depends on the amount of affinity which the carbon atoms of the nucleus have to offer to the substituents. In para-monosubstituted anilines, the diagonal bond between the substituted carbon atoms is the weaker the more unsaturated the substituting atom is, that is, the more affinity it can neutralise. An independent proof for this has been given by means of the directing influence on introduction of a substituent (*J. pr. Chem.*, 1905, [ii] **71**, 502). Whereas steric considerations would lead one to expect that the ratio of para- to ortho-compound would be

greater when bromobenzene than when chlorobenzene is nitrated, the reverse has been observed. It might be argued that this is due to the greater polarity of chlorine, which might inhibit the formation of an ortho-compound; but this view is excluded by the fact that other strongly negative groups, such as NO_2 and CO , which are mainly substituted in the meta-position, always yield more ortho- than para-di-derivatives as by-products. The only explanation that remains is therefore to assume that an unsaturated substituent, like chlorine, by making a great demand on the affinity of the carbon atom to which it is linked, primarily weakens the diagonal bond with the para-atom to a greater extent than the normal bonds with the ortho-atoms, with the result that the free affinity on which substitution depends is more increased in the para- than in the ortho-position; the reverse happens when an oversaturated atom, such as quinquivalent nitrogen in the nitro-group, is linked to the nucleus, which it cannot bind as strongly as the hydrogen atom that it has displaced. Moreover, since chlorine has a stronger para-substituting power, in similar conditions, than bromine, it must reduce the diagonal exchange of affinity to a greater extent, that is, it must be a little more strongly linked to the nucleus, a deduction which is in agreement with other facts and views briefly outlined in a recent preliminary note (Proc., 1909, 25, 261), also with the constants of chloro- and bromo-substituted aliphatic acids (Part I, tables).

If it follows, however, as a necessary deduction from observed facts, that the strength of the diagonal bond is variable, it remained an open question whether the transmission of a polar effect from atom to atom also varies with the amount of affinity bound by their linking. The affinity values of the chloro- and bromo-anilines are capable of supplying an experimental solution. For none of the meta- or para-compounds is there a steric factor to be considered. The quantitative factor would tend to make *p*-nitroaniline a stronger base than the meta-isomeride (Part I, tables); nevertheless, *p*-nitroaniline, where the strong negative influence is transmitted by a strong diagonal bond, is four times weaker than *m*-nitroaniline. On the other hand, taking the quantitative factor alone, the para-halogen-substituted anilines would be weaker than the meta-isomerides. From analogy to the nitroanilines, the polar factor would have the same effect if the transfer of polarity were independent of the strength of the diagonal bond. If, however, that transfer showed a variation parallel to that of the bond, it is conceivable that with a weakening of the diagonal linking, as in *p*-chloroaniline, a point may be reached where the diagonal influence becomes smaller than the

difference between the polar effects in the γ - and δ -positions in an open chain; in that case the polar factor becomes smaller for the para- than for the meta-position, and this difference may again conceivably be so great that it outweighs the quantitative effect in the opposite direction. The result would be that *p*-chloro- and bromo-aniline would be stronger bases than their isomerides. The same considerations enable one to foresee the relative strength of *p*-chloro- and *p*-bromo-aniline in either case. If the polar influence transmitted through a bond is independent of the strength of the latter, chlorine, being a little more strongly linked and also more polar, would, in the para-position, weaken aniline more than would bromine; in the reverse case, the very fact that chlorine is more strongly linked, would, by weakening the diagonal bond, also reduce its polar effect, so that *p*-chloroaniline might become a stronger base than *p*-bromoaniline. Moreover, if the polar factor outweighed the quantitative factor as regards the relative strength of the meta- and para-isomerides, it would have to do the same with regard to that of the para-compounds among each other. In other words, *p*-chloroaniline not only might, but would, be stronger than *p*-bromoaniline if *p*-chloroaniline were stronger than *m*-chloroaniline; the sequence of values of Lellmann and Götz, and of Veley, would therefore be impossible.

To decide these important points, it was necessary to devise a more trustworthy method for the determination of the affinity values of very weak bases. The vastly differing results quoted above show that no such method existed. It is well known that values based on electrical determinations of hydrolysis become less accurate for very weak bases, whereas the colorimetric methods depend greatly on physiological factors, and can claim but a qualitative usefulness. A good distribution method, however, which would yield values in agreement with those obtained by the conductivity method for stronger bases, where the latter method is trustworthy, could also be relied on to give accurate results for very weak bases, where the conductivity method fails. Such a method, simple and suitable also for organic laboratories, would be that due to Farmer and Warth (*loc. cit.*). The results published by these authors for *m*- and *p*-toluidine, however, differ considerably from those obtained by Bredig by the conductivity method (*loc. cit.*). This has been ascribed to association. Having had some experience of the difficulties affecting the quantitative determination of volatile amines, the author thought that the incorrect results of Farmer and Warth might be due either to actual experimental error in the determination of the amines, or to the too high concentrations used, which again may have been necessitated by

the difficulty of accurately estimating small quantities of the amine. As may be seen in the experimental part, this was found to be the case, and the introduction of an accurate method of determining the amine gave results in agreement with the determinations by conductivity where such were available, and closely agreeing with each other in all the other cases. The following values were obtained, at 25° and for $k_w=1.18$: *m*-toluidine, 5.48×10^{-10} ; *p*-toluidine, 1.48×10^{-9} ; *m*-chloroaniline, 3.45×10^{-11} ; *m*-bromoaniline, 3.82×10^{-11} ; *p*-chloroaniline, 9.9×10^{-11} ; *p*-bromoaniline, 8.8×10^{-11} . The relative values for *m*- and *p*-toluidine and those for *m*-chloro- and *m*-bromoaniline agree with the theory. The relative values for the meta- chloro- and bromo-compounds on the one hand, for the para-compounds on the other, constitute, on the basis of the present theory, an experimental proof that *atoms transmit their polarity to each other in proportion to the quantitative strength of the bond by which they are linked*. Lastly, the relative values for *p*-chloro- and bromo-aniline also agree with the theory.

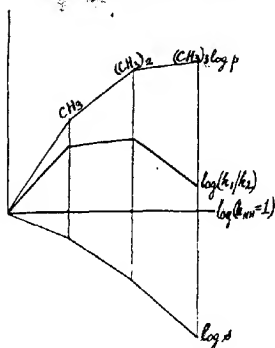
2.—Graphical Illustration of the Three Factors which Determine the Dissociation Constant.

When a radicle is introduced two or three times successively in the same position, the magnitude of the effect on each introduction is generally not the same. This is in accordance with the theoretical postulate that all three factors, if they differ from 1, must vary with each substitution. When two atoms A and B are linked, by partly transferring the polarity of each to the other, they reduce the difference in their specific polarities (compare Proc., *loc. cit.*). If a second atom B is then linked to A, the difference of polarity being now less than it was for the first B, the polar effect of the second B on A must be smaller than that of the first B. Similarly, since the force with which atoms are linked is the result of an equilibrium (*J. pr. Chem.*, 1907, [ii], 76, 185; Proc., *loc. cit.*), that equilibrium cannot be displaced so much by the second atom as by the first. The steric factor, on the other hand, shows the reverse change. The behaviour of di-ortho-substituted when compared with mono-ortho-substituted compounds, and that of tertiary, secondary, and primary aliphatic acids on esterification leave no room for doubt that the steric effect is relatively greater for each subsequent introduction of the same substituent in the same position.

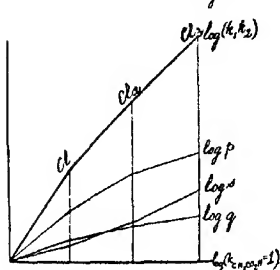
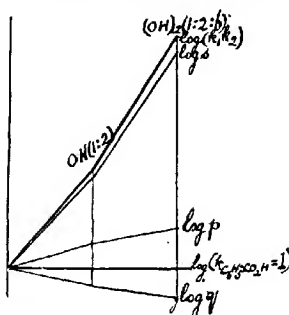
All this has been duly considered in the tables given in Part I, but it can, of course, be much more accurately represented graphically, as exemplified by the accompanying figures. The

logarithms of the factors and the total effect are plotted as ordinates, and the total number of substituting groups as abscissæ; the logarithms of the factors, when added, give the logarithm of the total effect exercised by a substituent. This total is the quotient of the dissociation constant of the substituted by that of the unsubstituted compound. The individual factors, although they cannot, of course, be determined with mathematical accuracy,

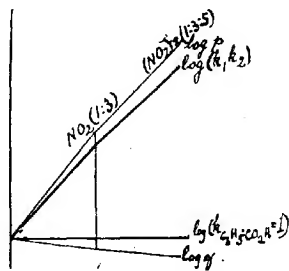
Substitution of Methyl in Ammonia.



Substitution of Hydroxyl in Benzoic Acid.



Substitution of Chlorine in Acetic Acid.



Substitution of NO₂ in Benzoic Acid.

can still be approximately arrived at, especially as regards their relative values, by conforming to the three postulates just mentioned, and by comparing a great number of compounds, and generally conforming to the principles laid down in Part I.

As the curves for ammonia show, the hitherto inexplicable effect of methyl in first raising, then lowering, the constant is readily accounted for. For trichloroacetic acid, the older value by

Ostwald ($K=121$) has been adopted, since the curves obtained with the constant given by Drucker ($K<40$) left no doubt that this value is too low, a conclusion which is supported by comparisons with other chlorinated acids. (Owing to the exigencies of space, the different figures are on different scales.)

3.—*The Constitution and Relative Stability of Some Quaternary Bases, Salts, and Ions.*

The constitution of numerous coloured organic salts is still a much discussed point, the question being generally whether the salts and ions have the same constitution as the corresponding base, or whether the ionisation of the latter has been accompanied by intramolecular rearrangement. In many cases, at least in solution, differences of constitution have been established; but in others only the inconclusive evidence afforded by the colour of the compounds has been available. The present theory suggests the following deductions.

A linking can be broken by ionisation if the amount of affinity available for its formation is relatively small (see Part I), or if the respective atoms are of pronounced and opposite polarity. Now the former of these conditions is common to all organic "halochromic" bases, both in their normal and pseudo-forms. In triphenylcarbinol, for instance, the aliphatic carbon atom of the benzenoid form is to a great extent saturated by the residual affinity of the three benzene nuclei (Thiele); little affinity is therefore left for the hydroxyl, which becomes ionisable (Walden). In the quinonoid form, the hydroxyl group would be attached to a carbon atom saturated by the great residual affinity of the atoms at the end of a chain of contiguous ethylenic linkings (compare pentadiene, Thiele), and therefore also weakly bound and ionisable. Hence it is evident that when such a compound is dissolved in an ionising solvent, the great mobility of the electric charge must cause an equilibrium in which ions of either form are present. The constant

$$k_1 = c_{\text{quinonoid ion}} / c_{\text{benzenoid ion}}$$

is determined mainly by the polarity of the atom linked to the positive corpuscle in either case, in the sense that the electron prefers the atom most strongly heteropolar or least isopolar to itself. Which of the two isomeric forms separates as a solid from such a solution depends on the product:

$$\frac{k_2 \times k_1}{k_2} \times \frac{\text{solubility of undissociated benzenoid form}}{\text{solubility of undissociated quinonoid form}} \quad (1).$$

If it is greater than 1, the quinonoid form separates, and vice versa. In this expression k_2 and k_3 are the dissociation constants

of the quinonoid and benzenoid forms respectively. These depend on the quantitative polar and steric factors, and their relative magnitude can therefore be ascertained by means of the present theory. It is seen that, whereas in the ion both forms are simultaneously present, the solid salt or hydroxy-compound may, a priori, correspond with either one of them.

When, the quinonoid form of two compounds, I and II, gives a base of alkaline strength (oxonium, azonium, etc.), and therefore practically non-hydrolysed salts, it can be shown that the relative degree of hydrolysis of their benzenoid salts, with strong acids and for equivalent dilutions, very approximately corresponds to the equation:

$$\frac{C_{\text{hydrolysed I}}}{C_{\text{hydrolysed II}}} = \sqrt{\frac{k_{2\text{II}} \times k_{1\text{II}}}{k_{2\text{I}} \times k_{1\text{I}}}} \quad (2).$$

The tendency toward hydrolysis therefore is also a function of all the three factors, as the following few examples may demonstrate.

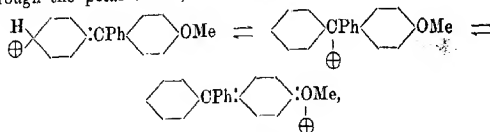
(a) *The Polar Factor.*—The dimethylamino-group is much more electropositive than methoxyl. In consequence, k_1 is much greater for *p*-dimethylamino-substituted triphenylcarbinols than for the corresponding methoxy-derivatives, and the former are hydrolysed to a much less extent than the latter. For the same reason, *N*-methylquinolinium salts are more stable than benzopyrilium salts. Since, for polar reasons, k_2 for a hydroxide or acetate, etc., is invariably much lower than for a chloride, sulphate, etc., whereas for the oxonium-, azonium-, etc., form, k_2 is of the alkaline order for the hydroxide as well as for all the salts, and since k_1 is independent of the anion, product (1) leads one to expect that the solid hydroxide, etc., will be benzenoid in many cases where the chloride, etc., are quinonoid.

(b) *The Quantitative Factor.*—An unsaturated substituent in the para-position raises the quantitative factor of k_2 , as shown by the formula:



An independent proof for this is afforded by the fact that in such cases groups attached to the methane-carbon atom become labile and reactive even where ionisation and a quinonoid change are excluded. Thus phenylisoamylcarbinol can be distilled at 132° (Grignard, *Ann. Univ. Lyon*, 1901, No. 6, page 1), whereas its *p*-dimethylamino-derivative gives off water at 120° (Sachs and Weigert, *Ber.*, 1907, 40, 4365), on account of the weakened linking of the hydroxyl group. When, accordingly, methoxyl is introduced into every para-position in triphenylcarbinol, each successive substitution

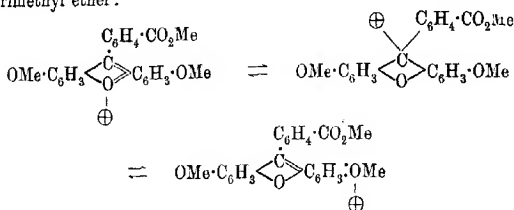
means, for the respective nucleus, a corresponding rise of k_3 , and, through the polar factor, also of k_1 . By equation (2), the suc-



Ionic equilibria.

cessive decrease of hydrolysis is therefore approximately geometrical (compare v. Baeyer and Villiger's "Potenzengesetz," *Ber.*, 1902, 35, 3021). Similar considerations apply to the introduction of one, two, and three dimethylamino-groups in the para-positions of triphenylcarbinol (Hantzsch and Osswald, *Ber.*, 1900, 33, 278), or of one and two of these groups in the para-position with respect to nitrogen in an azoxonium or azothionium salt (compare Kehrman, *Ber.*, 1906, 39, 923).

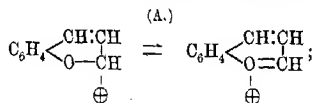
(c) *The Steric Factor.*—If the ionic equilibrium for fluor-trimethyl ether:



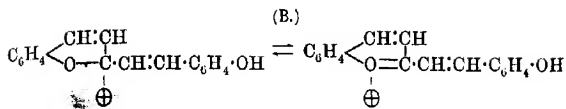
is compared with that for the similar compound not containing the carboxymethyl group, k_3 is nearly the same for both, since the steric and polar influence of the carboxyl group counterbalance each other. But k_1 , depending only on the polar factor, is much greater for the fluorescein, which is accordingly less hydrolysed, notwithstanding the presence of the additional negative substituent (Kehrman, *Ber.*, 1909, 42, 870).

It is a disputed point whether these and similar ions (azoxonium, azothionium, etc.) are ortho- or para-quinonoid; it is seen that they are both. The relative preponderance of the competing equilibria depends on the respective products k_1 and k_2 .

If the ionic equilibria for benzopyrylium salts are compared:

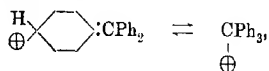


(A.)



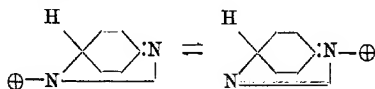
it is seen that for k_3 in B both the steric and quantitative factors are greater than in A; and the polar factor, and therefore k_1 , not being greatly different for A and B, B is hydrolysed to a less extent than A (Decker and Fellenberg, *Ber.*, 1907, **40**, 3818; Decker and Felser, *Ber.*, 1908, **41**, 3002).

In the ionic equilibrium,



an increase of the size of the anion raises the steric factor for k_3 ; accordingly, in these compounds the bromides are better conductors than the chlorides (Walden).

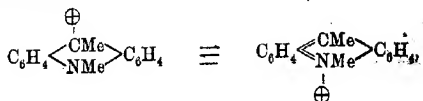
The above ionic equilibrium also facilitates the interpretation of the reactions of these compounds. If they were merely benzenoid in solution, the lability of para-substituting halogen atoms in dissociating solvents would be inexplicable; if a direct migration of the acidic radicle in the undissociated molecule were assumed to account for it (Gomberg), then triphenylmethyl chloride in sulphur dioxide would be transformed into *p*-chlorotriphenylmethane, since hydrogen is much more mobile than chlorine. According to the theory advanced in this paper, the exchange of halogen exclusively occurs in the quinonoid ion, and, the electric charge being much more mobile than hydrogen, the former only migrates to the central atom. It also follows from this that salts and double salts obtainable from a benzenoid carbinol or halogenide in a non-dissociating solvent must themselves be benzenoid, whatever their colour (compare v. Baeyer, Tschitschibabin). The same applies to the corresponding derivatives of distyryl ketone and similar compounds. These deductions apply to many other ionic equilibria, for instance: diazonium salts*:



* The reasons why Cain's formulæ have been adopted in this paper are, in addition to those adduced by Cain (Trans., 1907, 91, 1049, and recent discussion with Hantzsch), the following:

1. The fact that only the normal, but not the iso-derivative, can directly change to the diazonium form; this excludes stereoisomerism, and is explained by Cain's formula.

acridinium salts:



etc.

EXPERIMENTAL

In order to effect a quantitative estimation of the volatile amines obtained in the benzene layer by Farmer and Warth's distribution method, it is not feasible to precipitate the amine by hydrogen chloride and then to collect it. For, apart from partial thermic dissociation on drying, the mechanical losses preclude a sufficient accuracy, especially when it is remembered that the weight of the amine in the benzene layer, and therefore any experimental error in its determination, is multiplied by 20, after which the weight of the amine in the aqueous layer is obtained by subtraction.

(a) *Determination as Acetates.*—By adding a small excess of acetic anhydride to the benzene layer, and then distilling off the

2. The fact that only the isodiazohydroxide, but not the normal one, changes to a nitrosoamine excludes stereoisomerism, and is explained by Cain's formula.

3. The quantitative and polar factors being the same for *syn*- and *anti*-isomerides, but the steric factor being greater for the *syn*-, the latter would be the stronger acid. The reverse is, however, the case, notwithstanding the fact that the secondary change of the undissociated hydroxide, which would shift the electrolytic equilibrium in its favour, is generally more pronounced for the *iso*- than for the normal compound.

4. An objection against Cain's formula has now been removed by the recent discovery of azomethane, whereas no aliphatic diazonium compound has yet been obtained.

5. The fact that diazonium salts do not show the characteristic reactions of the ethylenic bonds of a quinone is in perfect harmony with Cain's views; according to universal experience, especially as regards benzene substitution, trivalent nitrogen is more unsaturated than an ethylenic linking, so that bromine, for instance, is first added by trivalent nitrogen, whereby the quinonoid configuration disappears, and a perbromide of Chattaway's formulation is produced. Similarly, hydrogen is first added by trivalent nitrogen in the diazonium ion, and the bridge being thereby opened, only a hydrazine, but not a diamine, can result. Oxygen, also, is primarily added by the trivalent nitrogen of the diazonium ion, the bridge being broken, and a nitroamine produced.

6. Other formulae that have been put forward seem to be highly improbable. There are steric objections against Euler's formula, whereas Morgan's seems an unnecessary complication. Cain's views leave room, of course, for an analogous ortho-quinonoid formula; but since Hantzsch (*Ber.*, 1903, 36, 2069; Hantzsch and Smythe, *Ber.*, 1900, 33, 505) has shown that the replacement of *o*- and *p*-substituents in the nucleus of diazo-compounds probably occurs in the isodiazo-form, it need not have any bearing on the constitution of the normal diazo- and diazonium compounds.

benzene and drying at 100° , the amine may be determined in a fairly exact way in some cases, whereas no constant weight is obtained in others. Thus, with *p*-bromoaniline, the weight of the acetyl derivative was invariably too low.

(b) *Determination as Hydrochlorides*.—The benzene was distilled off in a current of dry hydrogen chloride, and the residue, together with the flask (which had been weighed when dry), heated for an hour in a current of the same gas at 100° ; before opening the flask, the hydrogen chloride was expelled by dry carbon dioxide. At first a cork stopper was used, and two tests gave the following results:

p-Chloroaniline: 0.5774 gave 0.7394 hydrochloride; calculated, 0.7424; difference, 0.0030 = 0.4 per cent.

p-Chloroaniline: 0.4822 gave 0.6179 hydrochloride; calculated, 0.6199; difference, 0.0020 = 0.32 per cent.

Subsequently it was found that, after repeated use, traces of the cork dissolved in the benzene under the action of the acid, and a washing flask with ground-in stopper was therefore used.

(c) *Determination as Picrates*.—An experimentally simpler and, in view of reduced thermic dissociation, also better method consists in heating about 1 gram of picric acid to constant weight, at 100° , in a wide-necked 120 c.c. flask. The benzene solution is then introduced, the solvent distilled off, the flask heated for about forty-five minutes at 100° , and the weight of the amine obtained by subtraction. The flask is then heated for another hour, when the loss should be less than 0.0010 gram. If it is more, heating should be continued until it is less (per hour), and until the loss becomes constant (due to thermic dissociation only); this constant loss per hour, multiplied by the time of heating, must then be added to the final weight.

m-Bromoaniline: 0.0962 gave 0.0965 after heating for thirty minutes, and 0.0956 after seventy minutes.

p-Anisidine: 0.1166 gave 0.1169 after six hours; in this case prolonged heating was necessary, whereas nearly always forty-five minutes were sufficient, since, probably through traces of oxidation, the mass became coloured and tenaciously retained some benzene. As the anisidine picrate showed no thermic dissociation whatever, the weight became finally constant and was correct, notwithstanding the prolonged heating.

Since the picrate method gave results as accurate as could be desired, the results by that method are alone given in detail, those by the hydrochloride method being shortly mentioned for comparison. For *p*-anisidine, however (see Part III), the latter method was found to be preferable, there being no oxidation in that case.

Determination of Affinity Values.—In each case specially pure preparations were procured. The values were calculated by the formulæ given by Farmer and Warth (*loc. cit.*). The results by the picrate method do not vary by more than 5 per cent., a limit which has been declared by Ostwald to be admissible even for the direct conductivity method (*Zeitsch. physikal. Chem.*, 1889, 31, 73). They differ by less than 10 per cent. from Bredig's conductivity values, which, in one case, differ by 18 per cent. from each other.

The letters again signify: F =distribution coefficient; c_1 =initial concentration of acid; c_2 =total initial concentration of amine; x =hydrolysis; v =dilution; s =substance used (in grams); r =substance obtained from benzene layer. Where salt is added under s , the hydrochloride of the amine was used; in the other cases, the free amine and the amount of N -hydrochloric acid corresponding with c_1 were employed.

m-Toluidine.—A specimen was prepared from *p*-toluidine by acetylation, nitration, hydrolysis, elimination of the amino-group, and reduction:

	s .	r .	F .			
	0.1623	0.0907	31.9			
	0.0763	0.0428	32.06			
				Average, 32.		
	s .	r .	c_p .	c_1 .	v .	x .
0.9299 (salt)	0.0357	0.00648	0.00648	154.3	0.056	5.48×10^{-10}

Specimen from Kahlbaum, which was redistilled:

	s .	r .	c_p .	c_1 .	v .	x .
2.1794 (salt)	0.0561	0.0152	0.0152	65.8	0.037	5.46×10^{-10}
1.8753 (salt)	0.0518	0.0131	0.0131	76.3	0.0397	5.49×10^{-10}
				Average, 5.48×10^{-10} .		

By Hydrochloride Method:

$$s=1.59; v=67; x=0.0353; k=6.10 \times 10^{-10}.$$

p-Toluidine (Kahlbaum):

	s .	r .	F .			
	0.0952	0.0528	31.0			
	s .	r .	c_1 .	v .	x .	k .
2.6247 (salt)	0.0376	0.0183	0.0183	54.6	0.0207	1.48×10^{-9}

m-Chloroaniline (Schuchardt):

	s .	r .	F .			
	0.3316	0.2370	53.6			
	0.3169	0.2279	56.8			
				Average, 55.2.		
	s .	r .	c_1 .	v .	x .	k .
0.7793	0.2423	0.00613	0.00613	163	0.21	3.45×10^{-11}
0.7964	0.2465	0.00626	0.00626	160	0.208	3.45×10^{-11}
				Average, 3.46×10^{-11} .		

By Hydrochloride Method:

$$s=1.8143; v=70.4; x=0.142; k=3.56 \times 10^{-11}.$$

m-Bromoaniline (Schuchardt):

<i>s.</i>		<i>r.</i>	<i>F.</i>			
0.1916		0.1493	162.3	Average, 158.9		
0.3156		0.2449	155.5			
<i>s.</i>	<i>r.</i>	<i>c₂</i>	<i>c₁</i>	<i>v.</i>	<i>x.</i>	<i>k.</i>
0.2988	0.1673	0.00174	0.00175	575	0.345	3.73×10^{-11}
0.3397	0.1571	0.00163	0.00163	613.5	0.347	3.92×10^{-11}
(salt)				Average, 3.82×10^{-11} .		

By Hydrochloride Method:

$$s=0.3180; v=540.5; x=0.351; k=3.36 \times 10^{-11}.$$

p-Chloroaniline (Schuchardt):

<i>s.</i>		<i>r.</i>	<i>F.</i>			
0.2177		0.1478	84.0	Average, 64		
0.2030		0.1379	84.1			
<i>s.</i>	<i>r.</i>	<i>c₂</i>	<i>c₁</i>	<i>v.</i>	<i>x.</i>	<i>k.</i>
0.3173	0.1222	0.00498	0.00498	201	0.143	9.8×10^{-11}
(salt)						

By Hydrochloride Method:

$$s=1.9702; v=64.73; x=0.084; k=9.9 \times 10^{-11}.$$

p-Bromoaniline (Kahlbaum):

<i>s.</i>		<i>r.</i>	<i>F.</i>			
0.1929		0.1447	115.8	Average, 114.8.		
0.1908		0.1428	113.8			
<i>s.</i>	<i>r.</i>	<i>c₂</i>	<i>c₁</i>	<i>v.</i>	<i>x.</i>	<i>k.</i>
0.3443	0.1141	0.00165	0.00165	606	0.248	8.8×10^{-11}
(salt)						

By Hydrochloride Method:

$$s=2.0975; v=82.0; x=0.0975; k=9.2 \times 10^{-11}.$$

It will be noticed that by the picrate method, dilutions varying from 54.6 to 613.5 could be employed, whereas Farmer and Warth's dilutions were much smaller, varying from 10.0 to 64.1.

The author is again indebted to Dr. Senter for kind criticism.

FLEET, HANTS.

By Hydrochloride Method:

$$s=1.8143; v=70.4; x=0.142; k=3.56 \times 10^{-11}.$$

m-Bromoaniline (Schuchardt):

<i>s.</i>	<i>r.</i>	<i>F.</i>	
0.1916	0.1493	162.3	
0.3156	0.2449	155.5	Average, 158.9

<i>s.</i>	<i>r.</i>	<i>c₂</i>	<i>c₁</i>	<i>v.</i>	<i>x.</i>	<i>k.</i>
0.2988	0.1673	0.00174	0.00175	575	0.345	3.73×10^{-11}
0.3397	0.1571	0.00163	0.00163	613.5	0.347	3.92×10^{-11}
(salt)						Average, 3.82×10^{-11} .

By Hydrochloride Method:

$$s=0.3180; v=540.5; x=0.351; k=3.36 \times 10^{-11}.$$

p-Chloroaniline (Schuchardt):

<i>s.</i>	<i>r.</i>	<i>F.</i>	
0.2177	0.1478	64.0	
0.2030	0.1379	64.1	Average, 64

<i>s.</i>	<i>r.</i>	<i>c₂</i>	<i>c₁</i>	<i>v.</i>	<i>x.</i>	<i>k.</i>
0.3173	0.1222	0.00498	0.00498	201	0.143	9.9×10^{-11}
(salt)						

By Hydrochloride Method:

$$s=1.9702; v=64.73; x=0.084; k=9.9 \times 10^{-11}.$$

p-Bromoaniline (Kahlbaum):

<i>s.</i>	<i>r.</i>	<i>F.</i>	
0.1929	0.1447	115.8	
0.1908	0.1428	113.8	Average, 114.8.

<i>s.</i>	<i>r.</i>	<i>c₂</i>	<i>c₁</i>	<i>v.</i>	<i>x.</i>	<i>k.</i>
0.3443	0.1141	0.00165	0.00165	606	0.248	8.3×10^{-11}
(salt)						

By Hydrochloride Method:

$$s=2.0975; v=82.0; x=0.0975; k=9.2 \times 10^{-11}.$$

It will be noticed that by the picrate method, dilutions varying from 54.6 to 613.5 could be employed, whereas Farmer and Warth's dilutions were much smaller, varying from 10.0 to 64.1.

The author is again indebted to Dr. Senter for kind criticism.

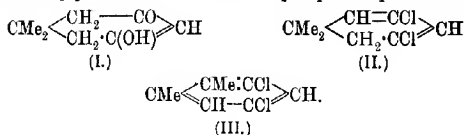
FLEET, HANTS.

XI.—3:5-Dichloro-o-phthalic Acid.

By ARTHUR WILLIAM CROSSLEY and GERTRUDE HOLLAND WREN.

IN a recent number of the *Berichte* (1909, 42, 3529), Villiger described the preparation of three of the four possible dichloro-o-phthalic acids (Cl:Cl, 3:6, 3:4, 4:5) by the direct chlorination of phthalic anhydride. Villiger points out (*ibid.*, p. 3532) that a fourth isomeride was described by Crossley and Le Sueur in 1902 (*Trans.*, 81, 1533), and regards the acid as 3:5-dichloro-o-phthalic acid, although "its constitution has never been controlled."

The acid described by Crossley and Le Sueur was prepared by the direct oxidation with dilute nitric acid of a substance believed to be 3:5-dichloro-o-xylene. This chloro-derivative (III) was obtained as a by-product in the action of phosphorus pentachloride on



dimethyldihydroresorcin (I) [the main product being 3:5-dichloro-1:1-dimethylcyclohexadiene (II)], and this structure was assigned to it because there did not appear to be any reason to presume that, in the conversion of the hydroaromatic into the aromatic dichloro-derivative, the chlorine atoms would alter their positions. During the reaction, however, a methyl group must have wandered, and this was shown to have migrated to the ortho-position, because on oxidation an acid was obtained which readily gave an anhydride, and also the fluorescein reaction. Villiger is right in saying that, at that time (1902), the constitution of the dichloro-acid had not been controlled either by an analytical or a synthetical method, but this check on the constitution has since been recorded.

In 1904 (*Trans.*, 85, 284) Crossley showed that the dichloro-o-xylene, obtained from dimethyldihydroresorcin, gave, on treatment with a nitrating mixture, a dichlorodinitro-o-xylene melting at 175—176°, and in 1909 (*Trans.*, 95, 205) Crossley and Renouf showed that this same dichlorodinitro-o-xylene could be obtained from 3:5-(or 4:6-)dinitro-o-xylene by reducing the two nitro-groups to amino-groups, replacing the latter by chlorine atoms, and nitrating the dichloro-o-xylene so obtained. This series of reactions obviously proved that the dichloroxylene obtained from dimethyldihydroresorcin is identical with that prepared by replacing the nitro-groups in 3:5-dinitro-o-xylene by chlorine atoms, and hence it must be

POWER AND MOORE: THE CONSTITUENTS OF COLOCYNTH. 99

3:5-dichloro-*o*-xylene. The properties of the two specimens of dichloro-*o*-xylene were not, however, carefully compared, nor was the dichloroxylylene, obtained from 3:5-dinitro-*o*-xylene, oxidised to the corresponding phthalic acid, but this has now been completed under similar conditions to those previously described, and the results are given in the following table:

	From dimethyl- dihydroresorcin.	From 3:5-di- nitro- <i>o</i> -xylene.
Dichloroxylylene	Yellow, refractive liquid; slight aromatic odour. B. p. 226°, m. p. 3—4°.	Yellow, refractive liquid; slight aromatic odour. B. p. 226°, m. p. 5—7°.
Dichlorodinitroxylylene	M. p. 175°—176°.	M. p. 176°.
Dichlorophthalic acid	M. p. 164° (previous soft- ening) with evolution of gas.	M. p. 164° (previous soft- ening) with evolution of gas.
Dichlorophthalic anhydride	M. p. 89°.	M. p. 89°.
Dichlorophthalanil	M. p. 150°—150.5°.	M. p. 150°.

In all cases the above melting points of the two corresponding series of substances were checked by the mixed melting-point method.

This direct synthesis of 3:5-dichloro-*o*-phthalic acid proves beyond doubt the correctness of the conclusions as to the constitution of the acid obtained by Crossley and Le Sueur from dimethyldihydroresorcin.

RESEARCH LABORATORY, PHARMACEUTICAL SOCIETY,
17, BLOOMSBURY SQUARE, W.C.

XII.—*The Constituents of Colocynth.*

By FREDERICK BELDING POWER and CHARLES WATSON MOORE.

UNDER the title of "Colocynth" the various national Pharmacopœias recognise the dried, peeled fruit, or the dried pulp of the fruit, of *Citrullus Colocynthis*, Schrader. Although this fruit has been used medicinally for a very long period, and has been the subject of several investigations, no complete chemical examination has hitherto been made of it, and the various products described in the literature as having been obtained therefrom were either amorphous or of an indefinite nature. It was recorded, for example, many years ago by Walz (*N. Jahrb. Pharm.*, 1858, 9, 16, 225; 1861, 16, 10) that colocynth contains a bitter glucoside, designated "colocynthin," which, although usually forming a yellow, amorphous mass, could be obtained in a crystalline state by the slow evaporation of its alcoholic solution.

This so-called colocynthin, to which the formula $C_{50}H_{84}O_{28}$ was assigned, was stated to yield, on heating with dilute acids, dextrose and "colocynthein," the latter having been described as an amorphous resin. The same investigator noted the occurrence of a tasteless, crystalline substance, designated "colocynthitin," which was found to be insoluble in water and cold absolute alcohol, but soluble in boiling alcohol and ether, although its characters do not appear to have been further determined. Henke (*Arch. Pharm.*, 1883, 221, 200) could obtain a product corresponding with colocynthin only in the form of a yellow, amorphous powder, and was unable to confirm the statement respecting its glucosidic character. Johannson (*Zeitsch. anal. Chem.*, 1885, 24, 154) has stated that "colocynthin, when heated with dilute sulphuric acid, yields colocynthein, elaterin, and bryonin," and he recorded some colour reactions which were supposed to differentiate these products.

Naylor and Chappel (*Pharm. J.*, 1907, [iv], 25, 117), in a paper entitled: "On *Cucumis trigonus*, Roxb., and Colocynthin," have compared a product obtained by them from the fruit of the above-mentioned species of *Cucumis*, indigenous to India, with the so-called "colocynthin" obtained from colocynth by Henke's method and by a modification of the latter. It is stated that whilst the product obtained from either the Indian fruit or from colocynth by Henke's process was amorphous, "that resulting from the modified process was most largely deposited on spontaneous evaporation of its solvent in pale yellow needles." They were thus led to conclude, in the first place, that "colocynthin prepared from *Citrullus Colocynthis* may be obtained in a crystalline state, despite the failure of Henke and of Wagner to induce it to assume a crystalline form"; secondly, that notwithstanding the doubts cast by Henke upon its decomposition by acids into colocynthin and a sugar, their results on the contrary confirm those of Johannson (*loc. cit.*), that colocynthin is capable of hydrolysis, and that it yields, amongst other products, colocynthein and elaterin, to which they may add—and a sugar, dextrose. The same authors furthermore state that "colocynth contains a white, crystalline body, agreeing in its general characters with the colocynthitin (colocynthitin) of Walz." There is, however, no evidence that any of the products prepared and examined by Naylor and Chappel were pure or homogeneous substances, and their comparison of them was chiefly restricted to certain colour reactions which are by no means characteristic of the substances they are supposed to identify. On the other hand, it may quite safely be assumed that the products referred to were very indefinite mixtures.

The present investigation has shown that colocynth contains a considerable amount of α -elaterin (*Trans.*, 1909, 95, 1889), which

is present in the free state, together with other compounds which have not previously been isolated. A complete summary of the results now obtained, with the deductions from them, is given at the end of this paper.

EXPERIMENTAL.

The material employed in this investigation was Turkish colocynth, consisting of the dried, peeled fruit of *Citrullus Colocynthis*, Schrader. The original weight of this material was 105 kilograms. After separating as completely as possible the seeds from the pulp, the latter was found to weigh 25.6 kilograms, or 24.4 per cent. of the whole. The seeds amounted to 79.3 kilograms, thus representing 75.5 per cent. of the weight of the entire peeled fruit.

A small portion (10 grams) of the above-mentioned pulp was subjected to the test for an alkaloid, when reactions were obtained indicating the presence of an appreciable amount of such a substance.

A further portion (20 grams) of the ground pulp was extracted successively in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100°, were obtained.

Petroleum (b. p. 35--50°)	extracted 0.33 gram	= 1.65 per cent.
Ether	" 1.75 "	" 8.75 "
Chloroform	" 1.06 "	" 5.30 "
Ethyl acetate	" 0.61 "	" 3.05 "
Alcohol	" 0.92 "	" 4.60 "

Total 4.67 grams = 23.35 per cent.

For the purpose of a complete examination, 24.6 kilograms of the ground colocynth pulp were completely extracted with hot alcohol. After the removal of the greater portion of the alcohol, a viscid, dark-coloured extract was obtained, amounting to 6.63 kilograms.

Distillation of the Extract with Steam.

A quantity (2 kilograms) of the above-mentioned extract, representing 7.42 kilograms of the pulp, was mixed with water, and steam passed through the mixture for several hours. The distillate, which amounted to 4 litres, contained some drops of oil floating on the surface. It was extracted with ether, the ethereal liquid being washed, dried, and the solvent removed, when a small quantity of an essential oil was obtained. This was a pale yellow liquid, which possessed a characteristic odour, and, after some time, deposited a small amount of a crystalline substance. The amount of this oil was, however, too small to permit of its further investigation.

Non-volatile Constituents of the Extract.

After the distillation of the extract with steam, as described above, there remained in the distillation flask a dark-coloured, aqueous liquid (A) and a quantity of a brown resin (B). The latter was collected and repeatedly washed with water until nothing further was removed, the washings being added to the above-mentioned aqueous liquid.

*Examination of the Aqueous Liquid (A).**Isolation of a New Dihydric Alcohol, Citrullol, $C_{22}H_{36}O_2(OH)_2$.*

The aqueous liquid (A), which amounted to 6.5 litres, was repeatedly extracted with ether, and the ethereal extracts united, after which a quantity of a colourless, sparingly soluble substance which accompanied them was separated by filtration.

This substance was almost insoluble in all the ordinary solvents, and appears to have been contained in the aqueous liquid in a colloidal form. It was, however, readily soluble in hot pyridine, from which it crystallised in glistening plates, melting and decomposing at $285-290^\circ$. The quantity so obtained was 0.9 gram:

0.1253 gave 0.3310 CO_2 and 0.1192 H_2O . $C = 72.0$; $H = 10.6$.

$C_{22}H_{36}O_4$ requires $C = 72.1$; $H = 10.4$ per cent.

This substance, when dissolved in chloroform with a little acetic anhydride, gave on the addition of a few drops of concentrated sulphuric acid a series of colour reactions similar to those produced by ipuranol, $C_{28}H_{48}O_2(OH)_2$ (Trans., 1909, 95, 249), and it appears, in fact, to be a lower homologue of the latter. As it does not agree in its properties with any substance of the above formula which has hitherto been described, it is proposed to designate it *citrullol*, with reference to the generic name of the plant from which it has been obtained.

It was ascertained that citrullol exhibits no physiological activity when administered to a dog in doses of 0.05 gram.

Diacylcitrullol, $C_{22}H_{36}O_4(CO \cdot CH_3)_2$.—This was obtained by heating citrullol with acetic anhydride, from which it separated in glistening needles, melting at 167° :

0.1330 gave 0.3378 CO_2 and 0.1098 H_2O . $C = 69.3$; $H = 9.2$.

$C_{26}H_{42}O_6$ requires $C = 69.3$; $H = 9.3$ per cent.

The ethereal liquid from which the citrullol had been separated by filtration, as above described, was subsequently evaporated, but it yielded only a resinous product from which nothing definite could be isolated.

Isolation of an Alkaloidal Principle.

The aqueous liquid, which had previously been extracted with ether, was treated with a solution of basic lead acetate. This produced a voluminous, yellow precipitate, which was collected, washed, and then suspended in water and decomposed by hydrogen sulphide. On filtering the mixture a liquid was obtained which, after acidifying with hydrochloric acid, responded to the ordinary alkaloid reagents. It was rendered alkaline by means of ammonia, and extracted many times with chloroform. The chloroform extracts were united and repeatedly shaken with dilute (10 per cent.) hydrochloric acid. The acid liquids were at once brought into a solution of ammonia, and the precipitated base extracted by means of chloroform. On the evaporation of the solvent there was obtained a small amount (about 5 grams) of a light brown product, which was resinous in character, very weakly basic, and possessed an extremely bitter taste. It dissolved sparingly in dilute acids, and was precipitated from its solutions by the usual alkaloid reagents, including tannin. Neither the free base nor its salts could be obtained in a crystalline condition. On warming the base with alkali hydroxides it dissolved, and, on prolonged boiling, ammonia was evolved. When heated with 20 per cent. hydrochloric acid it yielded ammonia and pyridine, the latter having been identified by its odour, and by the formation of its platinochloride.

The basic principle was not glucosidic, as no sugar was formed on boiling its acid solutions. It represents one of the physiologically active constituents of colocynth, as doses of 0.1 gram administered to dogs produced very drastic purgation.

The filtrate from the above-mentioned basic lead acetate precipitate was treated with hydrogen sulphide for the removal of the excess of lead, and the filtered liquid concentrated under diminished pressure to a small volume. It was then treated with a large volume of strong alcohol, which effected the precipitation of a quantity of inorganic salts, consisting chiefly of the chloride, sulphate, and nitrate of potassium, together with a little sugar. The latter yielded *d*-phenylglucosazone, melting at 208—210°. The clear alcoholic liquid was decanted from the precipitated material, mixed with purified sawdust, and the thoroughly dried mixture extracted in a Soxhlet apparatus with chloroform. This removed a small quantity of a brown syrup, which, on hydrolysis, yielded a sugar which readily reduced Fehling's solution, and from which *d*-phenylglucosazone, melting at 208—210°, was prepared. It is therefore evident that the aqueous liquid contained a very small amount of a glucosidic substance, but this could

not be obtained in a form which would permit of its being more definitely characterised.

Examination of the Resin (B).

Isolation of α -Elaterin.

This resin was a brown solid, which softened below 100° , and amounted to 675 grams. It was digested with about 2 litres of strong alcohol, in which it only partly dissolved. The undissolved portion was collected, washed first with alcohol, and then with ether, when it was obtained in small, colourless crystals, melting and decomposing at $227-230^{\circ}$. On recrystallising this product from alcohol, it formed small, glistening, hexagonal prisms, melting and decomposing at 232° . The amount of crystalline substance thus obtained was 80 grams, corresponding with about 1.08 per cent. of the weight of colocynth pulp employed:

0.1446 gave 0.3655 CO_2 and 0.1060 H_2O . $\text{C} = 68.9$; $\text{H} = 8.1$.

$\text{C}_{20}\text{H}_{28}\text{O}_5$ requires $\text{C} = 68.9$; $\text{H} = 8.0$ per cent.

$\text{C}_{24}\text{H}_{34}\text{O}_6$ " $\text{C} = 68.9$; $\text{H} = 8.0$ " "

$\text{C}_{28}\text{H}_{38}\text{O}_7$ " $\text{C} = 69.1$; $\text{H} = 7.8$ " "

This substance agrees in crystalline form, melting point, and solubility, and in all its chemical properties with α -elaterin, as previously described by us (Trans., 1909, 95, 1989). Its empirical formula cannot yet be considered definitely established.

A determination of its specific rotatory power gave the following result:

0.3121, made up to 20 c.c. with chloroform, gave $\alpha_D - 2.9^{\circ}$ in a 2-dm. tube, whence $[\alpha]_D - 68.9^{\circ}$.

The alcoholic solution of the resin (B), from which the α -elaterin had been separated by filtration as above described, together with the alcoholic and ethereal washings from the latter, was mixed with purified sawdust, the thoroughly dried mixture being then successively extracted in a Soxhlet apparatus with light petroleum (b. p. $35-50^{\circ}$), ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Resin (B).

Isolation of Hentriacontane, $\text{C}_{31}\text{H}_{64}$, and a Phytosterol, $\text{C}_{27}\text{H}_{46}\text{O}$.

This extract was a dark green, waxy solid, and amounted to 34 grams. It was dissolved in ether, the ethereal solution being successively shaken with dilute aqueous sodium carbonate and sodium hydroxide, which, however, removed nothing. The ether was accordingly evaporated, and the residue hydrolysed by boiling with an

alcoholic solution of potassium hydroxide, after which the alcohol was removed, water added, and the alkaline solution of potassium salts extracted with ether. The ethereal liquid was washed, dried, and the solvent removed, when a small quantity of a crystalline product was obtained. This was dissolved in 250 c.c. of absolute alcohol, and the solution kept for some hours, when a small quantity of an almost colourless substance separated. This was collected and washed with cold alcohol, after which it was distilled under diminished pressure. The distillate, which rapidly solidified, was crystallised from ethyl acetate, when small, glistening, colourless leaflets, melting at 68° , were obtained:

0.1344 gave 0.4176 CO_2 and 0.1824 H_2O . $\text{C} = 84.7$; $\text{H} = 15.0$.

$\text{C}_{21}\text{H}_{44}$ requires $\text{C} = 85.3$; $\text{H} = 14.7$ per cent.

The substance was thus identified as hentriacontane.

The alcoholic solution from which the hentriacontane had been removed by filtration was concentrated to a small volume and diluted with water, when a quantity of a crystalline substance separated. This was collected and washed with a little ethyl acetate, after which it was distilled under diminished pressure. The distillate was crystallised from a mixture of dilute alcohol and ethyl acetate, when it formed colourless, glistening leaflets, melting at 160 – 162° . The amount of substance so obtained was 1.3 grams:

0.2205, heated at 115° , lost 0.0104 H_2O . $\text{H}_2\text{O} = 4.7$.

0.1493 gave 0.4560 CO_2 and 0.1590 H_2O . $\text{C} = 83.3$; $\text{H} = 11.8$.

$\text{C}_{27}\text{H}_{46}\text{O}_2 \cdot \text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 4.5$ per cent.

$\text{C}_{27}\text{H}_{46}\text{O}$ requires $\text{C} = 83.9$; $\text{H} = 11.9$ per cent.

This substance thus agrees in composition with a phytosterol, and it yielded the colour reactions of this class of compounds. It was found to be optically inactive, and in this respect appears to differ from any of the phytosterols which have hitherto been recorded. The acetyl derivative, when crystallised from acetic anhydride, separated in glistening plates, melting at 175 – 177° .

Examination of the Fatty Acids.

The aqueous, alkaline solution of potassium salts, from which the hentriacontane and phytosterol had been removed by extraction with ether, was acidified and again extracted with ether. The ethereal solution was washed, dried, and the solvent removed, when a quantity (12 grams) of fatty acids was obtained which, when distilled under diminished pressure, passed over between 220° and $250^{\circ}/15$ mm. Ten grams of the mixed acids were converted into their lead salts, and the latter digested with ether, when the greater portion dissolved. Both the soluble and insoluble portions were decomposed by hydro-

chloric acid, and the regenerated fatty acids purified by distillation under diminished pressure. The soluble portion of the lead salts yielded 8 grams of liquid acids, whilst the insoluble portion gave 1.5 grams of solid acids.

The Liquid Acids.—These acids, when distilled under diminished pressure, passed over between 225° and $235^{\circ}/15$ mm. An analysis and a determination of the iodine value gave the following results:

0.1406 gave 0.3964 CO_2 and 0.1460 H_2O . $\text{C} = 76.9$; $\text{H} = 11.5$.

0.5625 absorbed 0.8346 iodine. Iodine value = 148.4.

$\text{C}_{15}\text{H}_{31}\text{O}_2$ requires $\text{C} = 76.6$; $\text{H} = 12.1$ per cent. Iodine value = 90.1.

$\text{C}_{18}\text{H}_{32}\text{O}_2$ „ $\text{C} = 77.1$; $\text{H} = 11.4$ „ „ Iodine value = 181.4.

In order to obtain more definite information respecting the nature of the above mixture, a quantity of it was oxidised according to the method described by Lewkowitsch (*Chemical Technology and Analysis of Oils, Fats, and Waxes*, 1904, Vol. I., p. 360). This resulted in the formation of dihydroxystearic acid (m. p. $125-127^{\circ}$) and tetrahydroxystearic acid (m. p. $157-160^{\circ}$), the latter in predominating amount.

It may thus be concluded that the liquid acids consisted chiefly of a mixture of oleic and linolic acids, the latter predominating.

The Solid Acids.—These acids melted at $56-58^{\circ}$, and, on analysis, gave the following result:

0.1430 gave 0.3955 CO_2 and 0.1636 H_2O . $\text{C} = 75.4$; $\text{H} = 12.7$.

$\text{C}_{16}\text{H}_{32}\text{O}_2$ requires $\text{C} = 75.0$; $\text{H} = 12.5$ per cent.

$\text{C}_{18}\text{H}_{36}\text{O}_2$ „ $\text{C} = 76.1$; $\text{H} = 12.7$ „ „

By repeated crystallisation from acetic acid a small amount of an acid melting at $68-69^{\circ}$ was obtained, from which a silver salt was prepared and analysed:

0.2118 gave 0.0576 Ag. $\text{Ag} = 27.2$.

$\text{C}_{15}\text{H}_{31}\text{O}_2\text{Ag}$ requires $\text{Ag} = 27.6$ per cent.

From the above results it is evident that the solid acids consisted of a mixture of palmitic and stearic acids.

Ether and Chloroform Extracts of the Resin (B).

These extracts amounted to 169 and 180 grams respectively. They were light-coloured resins, and, with the exception of about 10 grams of α -elaterin and a little of the previously-mentioned citrullol, nothing definite could be isolated from them. When heated with a solution of sulphuric acid in dilute alcohol they yielded no sugar, and therefore contained nothing glucosidic.

Both of the above-mentioned extracts were found to possess a very marked cathartic action, which was doubtless due in part to

the presence of small quantities of the previously described alkaloidal principle, as about 3 grams of the latter were obtained from them. The activity of the extracts was, however, not appreciably diminished by the complete removal of the alkaloidal principle, as they then produced drastic purgation when administered to dogs in doses of 0.1 gram.

Ethyl Acetate and Alcohol Extracts of the Resin (B).

These extracts were brown resins, amounting to 85 and 100 grams respectively, and nothing definite could be isolated from them. They were not glucosidic, and possessed no purgative action.

Examination of Colocynth Seeds.

The material required for the proceeding investigation of the pulp of colocynth fruit having rendered available a large quantity of the seeds, it appeared desirable to examine the latter with respect to their more important constituents.

A small portion (10 grams) of the crushed seed was tested for the presence of an alkaloid by treatment with Prollius's fluid, when distinct reactions were obtained with the usual reagents. These reactions were probably due to the presence of a very small amount of the same alkaloidal principle as that contained in the pulp of the fruit.

Separation of an Enzyme.

A quantity (2 kilograms) of the crushed seed was extracted by percolation with cold light petroleum for the removal of the fatty oil, after which the material was mixed with cold water and the mixture kept for several hours. The aqueous liquid was then expressed and filtered, and to it a quantity of strong alcohol was added. A voluminous, light-coloured precipitate was thus produced, which was collected, washed with a little alcohol, and dried in a desiccator. The product so obtained amounted to 10 grams, and, although containing a large proportion of inorganic material, it readily hydrolysed β -glucosides.

The Fatty Oil.

The amount of fatty oil contained in the seed, as determined by the extraction of 50 grams of the ground material in a Soxhlet apparatus with light petroleum (b. p. 35—50°), was 12.72 per cent.

The oil obtained was a clear pale yellow liquid, which was devoid of optical activity. A determination of its constants gave the following results: specific gravity, $20^{\circ}/20^{\circ} = 0.9273$; acid value, 2.6; saponification value, 186.7; iodine value, 126.6.

Hydrolysis of the Fatty Oil. Isolation of a Phytosterol, $C_{29}H_{54}O$.

A quantity (150 grams) of the oil was hydrolysed by boiling with alcoholic potassium hydroxide, the alcohol removed, water added, and the alkaline solution of potassium salts extracted with ether. The ethereal liquid was washed, dried, and the solvent removed, when a small quantity of a crystalline substance was obtained. This was distilled under diminished pressure, after which it was crystallised from a mixture of dilute alcohol and ethyl acetate, when it separated in colourless, glistening plates, melting at $158-160^{\circ}$. The amount of substance so obtained was 0.3 gram:

0.1700 gave 0.5154 CO_2 and 0.1724 H_2O . $C = 82.7$; $H = 11.3$.

$C_{29}H_{54}O$ requires $C = 82.8$; $H = 11.7$ per cent.

This substance was evidently a phytosterol, and it yielded the colour reactions of this class of compounds. A determination of its specific rotatory power gave the following result:

0.2473, made up to 20 c.c. with chloroform, gave $\alpha_D +0.12^{\circ}$ in a 2-dm. tube, whence $[\alpha]_D +8.1^{\circ}$.

The acetyl derivative, when crystallised from acetic anhydride, separated in glistening plates, melting at $167-170^{\circ}$.

The Fatty Acids.

The alkaline solution of potassium salts, which had been extracted with ether as above described, was acidified and again extracted with ether, the ethereal solution being washed, dried, and the solvent removed. The fatty acids thus obtained amounted to 87 per cent. of the weight of the oil. When distilled under diminished pressure, they passed over between 240° and $245^{\circ}/15$ mm. as a viscous liquid, which solidified on cooling to a soft, nearly colourless mass. A determination of the constants of the total acids gave the following results:

Melting point (complete fusion), $29.5-32^{\circ}$; specific gravity, $50^{\circ}/50^{\circ} = 0.8910$; neutralisation value, 195.6; iodine value 131.1.

These constants, both for the fatty oil and the total acids obtained therefrom, are in fairly close agreement with those recently recorded by Grimaldi and Prussia (*Chem. Zeit.*, 1909, 33, 1239). The last-mentioned investigators had, however, extracted the colocynth seeds by means of carbon tetrachloride, and describe the oil as having a reddish-yellow colour with a slight green fluorescence.

Summary.

The results of the preceding investigation may be summarised as follows:

The material employed consisted of the dried, peeled fruit of *Citrullus Colocynthis*, Schrader. The pulp of the fruit, deprived of its seeds, represented 24.4 per cent. of the whole.

On extracting the pulp with alcohol, and subjecting the resulting extract to distillation with steam, a very small amount of a pale yellow essential oil was obtained. From the portion of the extract which was soluble in water, the following substances were isolated: (i) A new dihydric alcohol, $C_{22}H_{36}O_2(OH)_2$ (m. p. 285–290°), designated as *citrullol*, which is apparently a lower homologue of ipuranol, and yields a *diacetyl* derivative melting at 167°. (ii) An amorphous, alkaloidal principle, which is a very weak base, and from which no crystalline derivative could be prepared; it possesses an extremely bitter taste, and represents one of the purgative principles of the fruit. The aqueous liquid from which the above-mentioned substances were isolated contained, furthermore, a quantity of inorganic salts, a little sugar, and a very small amount of an amorphous, glucosidic substance.

The portion of the alcoholic extract which was insoluble in water consisted chiefly of resinous material, from which, however, a quantity of α -elaterin (m. p. 232°; $[\alpha]_D - 68.9^\circ$) was isolated (compare Trans., 1909, 95, 1989). After the separation of the latter substance, the resin was extracted with various solvents, when it yielded a small amount of hentriacontane, $C_{31}H_{64}$ (m. p. 68°); a phytosterol, $C_{27}H_{46}O$ (m. p. 160–162°, optically inactive); a mixture of fatty acids, and a further quantity of α -elaterin, together with a little of the above-described alkaloidal principle. None of the extracts from the resin were glucosidic. The ether and chloroform extracts possessed marked purgative properties, even after the complete removal of the active alkaloidal principle.

The seeds of the colocynth, which represented 75.5 per cent. of the entire peeled fruit, were found to contain traces of an alkaloidal principle, a small amount of an enzyme which hydrolyses β -glucosides, and a quantity of fatty oil corresponding to 12.72 per cent. of the weight of the seed. The constants of the fatty oil, and of the total fatty acids obtained therefrom, were determined, and from the oil a small amount of a phytosterol, $C_{20}H_{34}O$, was isolated, which melted at 158–160°, and had $[\alpha]_D + 8.1^\circ$.

The results of the present research have established the fact that the so-called "colocynthin" and "colocynthitin," as well as the other products obtained from colocynth by previous investigators to which specific names have been attached, consisted of mixtures of a very indefinite character, and that the amount of glucosidic substance contained in the fruit is extremely small. On the other hand, it has now been ascertained that the purgative action of colocynth is due to

at least two principles, one of which is alkaloidal, although a very weak base, and apparently incapable of forming any crystalline salts, whilst the other source of activity is represented by some non-basic principle or principles contained in both the ether and chloroform extracts of the resin. All the attempts to obtain the last-mentioned active principle in a more definite form were, however, unsuccessful. No evidence could be obtained of the presence in colocynth of β -elaterin, which constitutes the physiologically active constituent of the fruit of *Ecballium Elaterium*.

In conclusion, the authors desire to express their best thanks to Dr. H. H. Dale, Director of the Wellcome Physiological Research Laboratories, for having kindly conducted the numerous physiological tests involved in this investigation.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

XIII.—*A Contribution to the Study of the Oxydases.*

By ROSS AIKEN GORTNER, Ph.D.

IN 1883 Yoshida (Trans., 1883, 43, 472) discovered laccase, the first of the oxydases to be studied. Later Bertrand (*Compt. rend.*, 1896, 122, 1215) found that another variety of this class was present in various examples of the vegetable world, for example, potatoes, bulbs of the dahlia, various mushrooms, such as *Russula nigricans*, etc. This oxydase differed radically from laccase in that it lost its vitality at 65–70°, and was also able to oxidise aqueous solutions of tyrosine through various colour stages (from pink to rose, violet, and blue-black), ending by a deposition of a black, melanin-like substance, and leaving the supernatant liquid completely decolorised. On account of this power of oxidising tyrosine, Bertrand gave the name tyrosinase to the oxydase.

Many authors* have since that time reviewed and extended the

Biedermann (*Pflüger's Archiv*, 1898, 72, 152); Biedermann and Moritz (*ibid.*, 1899, 75, 43); Gessard (*Ann. Inst. Pasteur*, 1901, 15, 593; *Compt. rend.*, 1903, 136, 631; 1903, 138, 774; *Compt. rend. Soc. Biol.*, 1902, 54, 1304, 1308); v. Fürth and Schneider (*Beitr. Chem. Physiol. Path.*, 1901, 1, 229); Durham (*Proc. Roy. Soc.*, 1904, 74, 310); Wilcock (*J. Physiol.*, 1908, 34, 207); Boudouy (*Trat. Sci. Univ. Rennes*, 1903, 2, 281; 1905, 4, 67); Gantier (*ibid.*, 1905, 4, 287); Weindl (*Arch. Entomol.*, 1907, 23, 632); Bertrand and Rosenblatt (*Compt. rend.*, 1908, 146, 304); Abderhalden and Guggenheim (*Zeitsch. physiol. Chem.*, 1908, 54, 337); Wolff (*Compt. rend.*, 1909, 148, 500; 149, 467); Bach (*Ber.*, 1909, 42, 591; *Biochem. Centr.*, 1909, 9, 1, 73); Roques (*Compt. rend.*, 1909, 149, 413).

original work, so much so that tyrosinases have been found to be very widely distributed in nature, and to occur not only in many plants, but also in numerous animal bodies.

By far the greater portion of the European work has been done with the glycerol extracts of *Russula nigricans* (Bertrand, *loc. cit.*), *Russula queletii* (Bertrand and Rosenblatt, *loc. cit.*), *Russula delicata* (Wolff, *Compt. rend.*, 1909, **148**, 500), *Russula noirissant* (Bertrand, *Ann. Inst. Pasteur*, 1908, **22**, 381), etc., but the occurrence of tyrosinase has been demonstrated in the ink sac of the squid (Przibram, cited by v. Fürth, *Vergleichende chemische Physiologie der niederen Tiere*, Jena, 1903, p. 372; Gessard, *Compt. rend.*, 1903, **136**, 631), in the hameolymph of various insects (v. Fürth and Schneider, *loc. cit.*), in wheat bran (Bertrand and Mutermilch, *Ann. Inst. Pasteur*, 1907, **21**, 833), in the intestinal fluid of meal worms (*Tenebrio molitor*) (Biedermann, *loc. cit.*), in molluscs (Biedermann and Moritz, *loc. cit.*), in gum arabic and mistletoe (Bonducy, *loc. cit.*), and in plants which blacken during the process of drying (Gautier, *loc. cit.*), etc., etc.

Miss Durham (*loc. cit.*) states that she obtained evidence of the presence of tyrosinase in the skins of foetal and newly-born guinea pigs and rabbits of black or agouti origin. Inasmuch as her results depended on the addition of a milligram of ferrous sulphate as an "activator" (no darkening occurring in a tube containing "juices" and tyrosine but no ferrous sulphate), and, as will be shown later in this paper, a milligram of ferrous sulphate inhibits coloration almost completely—also since her "tyrosinase" (obtained from red guinea pigs) is the only known example of a tyrosine oxidising ferment which oxidises only to the orange stage (all others progressing to black), and lastly, since the pigment-like substances described in her work "are readily soluble in alkalis," unlike those produced by v. Fürth and Schneider (*loc. cit.*), and also by the author from the interaction of tyrosine and tyrosinase, these substances being found to be insoluble even in hot dilute sodium hydroxide or ammonia, it is apparent that her "tyrosinase" reaction, if not due to some section of the ferrous sulphate, is certainly due to an agent altogether distinct from that named by Bertrand "tyrosinase." The author has made several attempts to confirm her results, but has as yet obtained no trace of coloration induced by an oxydase.

In all the literature cited, the tyrosinase was that obtained by extracting with either glycerol or chloroform-water. Gessard (*Ann. Inst. Pasteur*, 1901, **15**, 601) states that the extract may be made with either chloroform-water or glycerol, but that the glycerol extract keeps best, and has no effect on the results.

The source of the tyrosinase in the experiments described in this paper varied somewhat, but the major portion of the work is devoted to the description of a new variety of this ferment, which is distinguished by absolute insolubility in water, the activity of which is destroyed by glycerol, by alcohol and ether, or by drying at room temperature; further, it does not oxidise resorcinol, orcinol (Wolff, *loc. cit.*), pyramidone (Bondouy, *loc. cit.*), or quinol, thus in most of these reactions differing radically from the known tyrosinases.

EXPERIMENTAL.

Tyrosinase in the Intestinal Fluid of the Meal Worm (Tenebrio molitor).

Biedermann (*loc. cit.*) in 1898 made a detailed study of the meal worm (*Tenebrio molitor*), and he states that "the middle intestines of three or four hungry worms were triturated with chloroform-water. On allowing the yellow solution to stand overnight with tyrosine, a violet-black coloration was produced, whilst in a solution to which no tyrosine had been added only a slight darkening was observed."

In a repetition of the work, his results have been confirmed by the author, but it has also been found that the more perfectly the body solids were removed from the outer surface of the intestine the less rapidly did the coloration with tyrosine proceed, this being true for either hungry or well-fed larva. The body of the larva is filled with a white semi-solid folded in many convolutions. If this solid is exposed to the air, it rapidly changes through slate to a dense grey-black, and, as will be shown later, it contains some soluble tyrosinase and a large amount of a new "insoluble tyrosinase."

The intestinal juice, obtained by removing the intestine and cleansing it as completely as possible from the body-filling, then grinding with fine quartz in an agate mortar, triturating with chloroform-water, and filtering, does not colour appreciably in twenty-four hours, but later changes through violet to a dense black solution. The action of the fresh extract on tyrosine is slow, but shows the presence of some small amounts of the oxydase; that the oxidising power is due to incomplete removal of the body-filling and not to intestinal juices is the present belief of the author.

Soluble Tyrosinase in the Body-Filling of the Meal Worm.

Twenty-seven grams of the larva were ground in a mortar with chloroform-water, and the milky liquid was strained through

cheese-cloth. The grinding of the residue was repeated until the strainings were no longer milky, and only the hulls of the larva remained in the cloth.

The milky extract, if kept a short time in the air, rapidly darkens at the surface, but remains white where not in contact with oxygen.

The extract was poured into a thin filter paper, and kept, covered with a watch glass, until most of the liquid had filtered through, dropping on solid ammonium sulphate in excess of what was required to produce a saturated solution, this process requiring some hours. In this manner the soluble tyrosinase and the colloidal insoluble tyrosinase, which passed through the first filter, were precipitated together as a light grey, voluminous mass.* This was collected, washed with saturated ammonium sulphate solution, dissolved in distilled water and filtered, reprecipitated with ammonium sulphate, washed with a saturated ammonium sulphate solution, and dissolved in 40 c.c. of 0.05 per cent. sodium carbonate solution, and filtered. The solution so obtained was light brownish-grey, and contained the soluble tyrosinase originally present in the larva. 0.5 c.c. portions of this solution were added to solutions of various reagents, with the results shown in table I. When the tyrosinase solution had been previously heated to 90°, no coloration appeared in any tube, excepting in that containing quinol, showing that perhaps two oxydases were present, tyrosinase being destroyed before 90°, and laccase perhaps surviving the short heating, tyrosinase being almost always accompanied by a laccase-like ferment (Bourquelot, *Compt. rend.*, 1896, **123**, 315, 423).

TABLE I.

Action of Soluble Tyrosinase from Larva of Tenebrio molitor.

Tube.	Reagent.	Total volume, in c.c.	Time, in hours.	Results.
1.	—	3	72	Unchanged.
2.	Tyrosine	3	24	Violet-black and precipitate.
3.	Tyrosine + 0.001 gram FeSO ₄	3	72	Unchanged.
4.	Quinol	3	24	Deep red.
5.	Phenol	3	48	Pink.
6.	p-Aminophenol	3	24	Brownish-black.
7.	Guaiacol	3	24	Pink.
8.	Phloroglucinol	3	72	Unchanged.
9.	Resorcinol	3	72	"
10.	Pyramidone	3	72	"

* If the filtered liquid is not precipitated, it very rapidly darkens and soon becomes jet black. The black pigment may be salted out with ammonium sulphate and appears as a lustrous, black, amorphous mass. It will be investigated later.

When the precipitation of the filtrate is carried out by the addition of three volumes of alcohol instead of saturating with ammonium sulphate, a grey precipitate is obtained very similar in appearance to that produced by the ammonium sulphate, but when this precipitate is dissolved it shows no tyrosinase properties, and only the laccase-like ferment can be found in the alcoholic mother liquor, showing that apparently alcohol is fatal to this variety of tyrosinase.

Insoluble Tyrosinase.

The residue left on the filter from the filtration of the extract of crushed larva (see above) was washed on the filter with chloroform-water during several days. The washing was considered complete when 10 c.c. of the liquid, which had been in contact with the solid (total volume=60 c.c.) for sixteen hours, after being filtered through double "barium" filters, gave no coloration with tyrosine during twenty-four hours.

The solid so obtained is a grey, flocculent mass, which, when dried at 65°, forms 4 to 5 per cent. of the original weight of the live larva. It contains from 1.0 to 1.5 per cent. of ash, consisting chiefly of iron oxide, and containing no manganese which could be detected by the usual tests. The drying process, however, destroys all oxidising activity.

The entire insoluble mass, naturally, cannot be called tyrosinase, as a large percentage of it must be other insoluble body products. The insoluble tyrosinase in this preparation is, however, very active. If the product is washed as above, it may be kept without diminution of activity for months in a tube containing enough chloroform and water ($1\text{CHCl}_3:4\text{H}_2\text{O}$) to cover it completely. When a few drops of this suspension are added to an aqueous solution of tyrosine, the mixture undergoes a series of colour changes, ranging through pink, rose, violet, and blue-black to a deposition of a black, pigment-like substance, and leaving the supernatant liquid completely decolorised. The coloration usually begins in from two to four minutes after the addition of tyrosine, and the series of colour changes is complete in a few hours. If the colourless, supernatant liquid is then removed and more tyrosine solution added, the series of colour changes is repeated. This continual removal and addition of tyrosine solution has been carried out with one specimen of tyrosinase weighing approximately 0.01 gram* for four days, during which the series of colour changes was repeated seven times.

* Where weights of "insoluble tyrosinase used" are given, it means that an aliquot portion of the preparation was dried on a water-bath and weighed. The weights are therefore only an approximation.

That the entire series of colour changes is produced from contact with the insoluble portion and not by a zymogen acting in the presence of tyrosine to set free soluble tyrosinase, was proved by the following experiment.

A portion of insoluble tyrosinase was added to a saturated aqueous solution of tyrosine. In a few minutes the solution had become pink, changing shortly to rose. One half of this solution was now removed and filtered twice through "barium" filters, the other half remaining in contact with the insoluble tyrosinase. The tubes were then set aside in the dark. In a few hours the contents of the tube containing the insoluble tyrosinase and tyrosine solution became changed, first violet, and finally colourless, with the deposition of a black, pigment-like substance. The filtered portion, on the other hand, remained an unchanged rose colour for eighteen days, and was then discarded.

That the tyrosinase was not present in still unruptured cells was proved by grinding the insoluble preparation in an agate mortar with fine quartz until no grit was precipitable. This was then triturated with water, and filtered. The filtered portion gave no coloration with tyrosine in twenty-four hours, whilst the insoluble residue was as active as it was before grinding.

Not only does the insoluble preparation oxidise tyrosine easily, but other phenolic compounds are also acted on to produce the series of colour changes given in table II:

TABLE II.

Approximately 0.01 gram of insoluble tyrosinase (+ insoluble body products) was used in each test. Volume of 5 c.c. in each.]

Tube.	Reagent added.	Colour series.
1.	—	Colourless after 72 hours.
2.	Tyrosine	Pink → orange-rose → rose → light red → violet → blue-black → insoluble black precipitate.
3.	Pyrogallol	Colourless after 72 hours.
4.	Phloroglucinol	" " "
5.	Resorcinol	" " "
6.	Quinol	" " "
7.	Pyramidone	" " "
8.	Orcinol	" " "
9.	p-Aminobenzaldehyde ...	" " "
10.	p-Nitrosobenzaldehyde ...	" " "
11.	Ethyl p-aminobenzoate...	" " "
12.	p-Aminophenol	Brown → reddish-brown precipitate.
13.	Guaiacol	Orange-pink → red → brownish-red.
14.	Gum guaiacum	Rapidly blues.
15.	2:4-Diaminophenol * ...	Pink → orange-pink → orange-brown → orange-red → deep red.

* An aqueous solution of 2:4-diaminophenol changes colour when exposed to the air, but not nearly so rapidly as when insoluble tyrosinase has been added.

In order to test the effect of salts on the system tyrosine-tyrosinase, 0.001 gram of various salts was added to tubes containing approximately 0.01 gram of insoluble tyrosinase and 5 c.c. of a saturated aqueous solution of tyrosine, and the tubes were kept for some time.

In those tubes to which had been added potassium cyanide, mercuric chloride, copper sulphate, uranyl chloride, and ferrous sulphate, no coloration was observed during sixteen hours. The addition of manganous sulphate, potassium nitrite, barium chloride, potassium oxalate, strychnine, or atropine had no effect on the progress of the coloration, whilst sodium arsenate, starch, and starch and potassium iodide had a marked effect in that the rose coloration appeared more rapidly and remained much longer and deeper in colour than in the case of the untreated solution. The portion treated with starch and potassium iodide became intense red,* whilst the untreated solution was only light pink. Warming the solution to 75° for a short time prevents all coloration when it is subsequently treated with tyrosine, starch, and potassium iodide.

Action of Glycerol on Insoluble Tyrosinase.

Various attempts were made to preserve the ferment in glycerol rather than in chloroform-water since Gessard (*loc. cit.*) recommends this method, but in every instance the preparation was rendered inactive. In order further to test the effect of glycerol, the author proceeded as follows. One gram of live larva was ground with chloroform-water and filtered through cheese-cloth. To the filtrate (3 c.c.) was added two volumes of glycerol and solid tyrosine. No coloration appeared in twelve hours. The solution was then diluted with water to 36 c.c., and kept for a further period of twenty-four hours without a trace of coloration appearing; a further dilution to 65 c.c. caused no change in seventy-two hours more. Without the addition of glycerol the coloration proceeds very rapidly even in the absence of added tyrosine. Addition of glycerol to the washed insoluble tyrosinase and keeping the mixture for a few hours caused a total loss of the activity of the preparation even when subsequently washed free from glycerol.

Occurrence of a Laccase-like Ferment in the Larva of Tenebrio molitor.

It was early noticed in the progress of this work that quinol was rapidly oxidised by the unwashed body-filling of the larva and

* No iodine was liberated in 43 hours.

not by the washed insoluble tyrosinase. If the washings are heated rapidly to boiling, the resulting precipitate collected, and the filtrate then evaporated at 30–40°, an oily solid is deposited which is very active in oxidising quinol, but does not affect tyrosine. This oxydase is much more resistant to heat than tyrosinase, and may be heated at 100° for some minutes without losing much of its activity. Prolonged heating, however, gradually causes it to lose its oxidising power.

The Chromogen occurring in the Larva of Tenebrio molitor.

As has been previously stated, the body fluid of the meal worm, when exposed to the action of the air, rapidly darkens under the influence of the tyrosinase contained in it and oxygen, to form a dense, black solution. The formation of this coloration shows that a chromogen must be present in the body-filling of the larva, and attempts were made to isolate it.

Five grams of the larva were ground with chloroform-water and filtered through cheese-cloth. The filtrate (150 c.c.) was warmed in a water-bath to 85° to destroy all tyrosinase and to coagulate the insoluble products, albumen, etc. After a few minutes' heating, the mixture was filtered, and the filtrate precipitated with basic lead acetate, again filtered, and lead removed from the filtrate by hydrogen sulphide. The clear filtrate was evaporated to dryness in a water-bath. The product, so obtained, is a light yellow resin, completely soluble in 0.05 per cent. sodium carbonate (3 c.c.), giving a yellow solution. When three drops of this solution are added to water, containing insoluble tyrosinase (total vol. 2 c.c.), a mixture is obtained giving identical colour changes to those obtained from a tyrosine solution, namely, pink, through rose, violet, and blue-black, a black precipitate being finally formed. The amount of the chromogen so obtained was very small, but an attempt will be made to prepare larger quantities in the near future. From the evidence at hand, however, the chromogen appears to be either tyrosine or a closely allied compound. No coloration is produced by the addition of laccase.

Occurrence of Tyrosinase in Other Animal Bodies.

Two examples of myriopods, *Scalopocryptops sexpinosa* and *Julius canadensis*, Newp., were examined for the presence of tyrosinase, and in both instances an abundance of the ferment was found. The entire body was ground with sand in an agate mortar, extracted with chloroform-water, and filtered. This fluid was divided into three parts, one containing no added material, one

tyrosine, and one phenol. In a few hours the portion containing tyrosine had changed through violet to blue-black, with the deposition of a black, melanin-like substance. The portion containing phenol changed through orange to deep sepia, whilst the untreated tubes remained colourless. Boiling prevents all coloration.

Tyrosinase was also found to be very abundant in the larva of *Cucujus clavipes*,* changing tyrosine solution through pink to rose, violet, blue-black to melanin, and phenol through rose to light red and crimson.

Occurrence of a Quinol-oxidising Ferment in Vertebrate Animal Tissues.

It has long been observed (Baumann and Preusse, *Zeitsch. physiol. Chem.*, 1879, 3, 156) that after the use of phenol the urine assumes a dark colour on exposure to the air (the so-called "carbolic urine"), from which quinol, quinolsulphonic acid, and quinol-decomposition products may be isolated. The same coloration occurs after the administration of quinol.

The author has observed that this coloration is not peculiar to the urine, but that extracts of practically all the tissues rapidly oxidise quinol to intensely coloured solutions. Among the animals investigated were young rats, mice, albino rats, kittens, chickens, etc., and in each instance a rapid oxidation was produced with extracts of the heart, liver, lungs, brain, kidneys, spleen, pancreas, testes, ovary, skeletal muscles, skin, and blood serum; in every case the coloration being most intense when blood serum was used. Long-continued boiling causes a gradual loss in oxidising power, although a very short heating seems to increase the activity.

Different extracts gave different colorations in similar circumstances, and these changes are shown in table III. The tissues were ground with sand, triturated with chloroform-water, and filtered. To the turbid filtrate, quinol was added, and the tube set aside in an oven at 40°.†

No coloration was observed in any case in "blank" tubes, or in tubes treated with tyrosine or guaiacol. In all cases the final coloration obtained with quinol was either deep blood-red or reddish-brown verging on black.

When quinol was injected subcutaneously in a kitten, and the animal killed after three to four hours, the post-mortem examination showed a red circle under the skin where the injection was

* Identified through the courtesy of Dr. A. D. Hopkins, of the Bureau of Entomology, The United States Department of Agriculture.

† The coloration is decidedly more rapid at 40° than at room temperature.

TABLE III.

Tube.	Organ.	Origin.	Time, in hours.	Result.
1.	Skin	Young rat ...	12	Claret-coloured solution.
2.	"	" " ...	24	Deep red solution.
3.	"	Albino rat ...	24	" "
4.	"	" " ...	24	Brown solution (had been first heated to 100°).
5.	Spleen.....	" " ...	24	Red solution.
6.	Kidney	" " ...	24	Rose " (after 48 hours, red).
7.	Pancreas.....	" " ...	48	Rose solution.
8.	Lungs	" " ...	48	" "
9.	Liver	" " ...	48	" "
10.	" (boiled)...	" " ...	48	Light pink solution.
11.	Testes	" " ...	48	Deep red "
12.	Muscle	" " ...	48	Pink "
13.	Brain	" " ...	48	Deep brown "
14.	Bile.....	Chicken	16	Brown "
15.	"	"	24	Black "
16.	Liver	"	16	Deep red "
17.	Brain	"	16	Reddish-brown solution
18.	Ovary	"	16	" "
19.	Blood serum ..	"	16	Reddish-black "
20.	Pancreas.....	"	16	Brownish black "
21.	Spinal cord.....	Grey rat	16	Bright red "
22.	Brain	"	16	Dull reddish-brown solution.

made. The remainder of the under surface of the skin and the flesh were normal in colour, but on exposure to the air the skin tissue and the muscles rapidly turned pink. The blood-serum also soon became deep red, although, when expressed from the clot, it was of normal colour.

Occurrence of Laccase and Tyrosinase in the "Indian Pipe"
(*Monotropa uniflora*).

Gautier (*loc. cit.*) found that many plants which blacken during the process of drying contain a tyrosine-oxidising ferment. The common *Monotropa uniflora*, of the north-eastern portion of the United States, presents this peculiarity, and an effort was made to discover whether or not this plant could be used as a source of tyrosinase.

A chloroform-water extract of the crushed plants was precipitated with five volumes of 95 per cent. alcohol. The violet-coloured precipitate so obtained was collected after twenty-four hours, and redissolved in 0.05 per cent. sodium carbonate solution. The solution was found to have some oxidising power, slowly oxidising tyrosine to a blue-black insoluble substance. The action on quinol was very rapid, however, the solution becoming deep red. Boiling destroyed the power of oxidising tyrosine, but not

the power of oxidising quinol, showing that the major portion of the oxydase is evidently laccase. Tincture of gum guaiacum is rapidly turned blue, whilst guaiacol is turned pink by the action of the solution.

If the fresh plants are crushed with three parts by weight of glycerol, and the mixture kept for eighteen hours and then filtered by the aid of the pump, a clear, greenish-blue solution is obtained, which, after a long time, becomes an intense bluish-black.

Two drops of this filtrate almost instantly turns tincture of gum guaiacum blue, and oxidises tyrosine, which changes colour through pink to rose, violet, and finally blue-black. Quinol exhibits, under its influence, colour changes from orange to brown, deep reddish-brown, and finally intense red. When the solution of the oxydase has previously been warmed to 80°, it is without effect on tyrosine solution. From these data, it is evident that both tyrosinase and laccase are present in the plant, but the quantity of tyrosinase is small compared with that found in certain of the *Russula*.

Summary.

1. A new variety of tyrosinase has been discovered and investigated.

2. This variety is distinguished from the known tyrosinases by its insolubility in water, its loss of vitality in glycerol solutions and on drying, and by its inability to oxidise resorcinol, orcinol, etc.

3. A chromogen has been found in the larva of *Tenebrio molitor*, giving with tyrosinase colour reactions identical with those given by tyrosine.

4. Tyrosinase has been found in the myriopods *Scalopocryptops scarpinosa* and *Julius canadensis*, Newp., and also in the larva of *Cucujus clavipes*.

5. It has been observed that extracts of almost all animal tissues possess the power of oxidising solutions of quinol, and that this power is considerably diminished by prolonged boiling.

6. Tyrosinase has been found to exist together with laccase in the *Monotropa uniflora*.

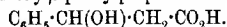
THE CARNEGIE INSTITUTION OF WASHINGTON,
COLD SPRING HARBOUR,
LONG ISLAND, NEW YORK, U.S.A.

XIV. ~~Experiments on the~~ *Experiments on the Walden Inversion. Part III.*
Optically Active β -Hydroxy- β -phenylpropionic Acids
and the Corresponding β -Bromo- β -phenylpropionic
Acids.

By ALEX. MCKENZIE and HERBERT BROOKE PERREN HUMPHRIES.

THE effect, which in certain cases is associated with the electro-negative phenyl group, has been brought out clearly in previous work on the Walden inversion (McKenzie and Clough, *Trans.*, 1908, 93, 811; 1909, 95, 777). For example, *l*-phenylchloroacetic acid, $C_6H_5 \cdot CHCl \cdot CO_2H$, is converted into a mixture of *r*- and *l*-mandelic acids when aqueous sodium hydroxide is used to displace the chlorine atom by the hydroxy-group; a mixture of *r*- and *d*-mandelic acids is, however, produced when silver carbonate is substituted for sodium hydroxide. This behaviour makes the problem of the Walden inversion more complicated than before, for this reason that, by analogy with previous work of Walden and others, it was to have been expected that sodium hydroxide should have caused the formation of a *dextro-rotatory* mandelic acid mixture from the *levorotatory* chloro-acid, and that silver carbonate should have caused the formation of a *laevo-rotatory* mandelic acid mixture. The contrast between the interconversion of the active lactic acids, $CH_3 \cdot CH(OH) \cdot CO_2H$, on the one hand, and the interconversion of the active mandelic acids, $C_6H_5 \cdot CH(OH) \cdot CO_2H$, on the other, by the Walden inversion, is very striking, and must be taken into account in any interpretation regarding the mechanism of the action which may be advanced.

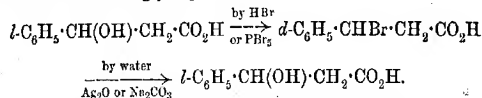
The present research is concerned with changes undergone by the optically active β -hydroxy- β -phenylpropionic acids,



One of the objects was to find out if any Walden inversion could be detected in the course of changes undergone by a compound where the carboxyl group is not attached directly to the asymmetric carbon atom. Meanwhile this problem has been investigated by E. Fischer and Scheibler (*Ber.*, 1909, 42, 1219), who studied the displacement of the hydroxy-group in *l*- β -hydroxybutyric acid, $CH_3 \cdot CH(OH) \cdot CH_2 \cdot CO_2H$. By the action of phosphorus pentachloride, this acid was converted into *d*- β -chlorobutyric acid, from which the original *l*-hydroxy-acid was regenerated by displacing the chlorine by means of a number of different agents.

Bearing in mind the possibility of the phenyl group exerting an influence entirely different from that of the methyl group, we prepared the optically active β -hydroxy- β -phenylpropionic acids by the resolu-

tion of the inactive acid with morphine in aqueous solution. When the *l*-acid is acted on by hydrobromic acid, the resulting bromo-acid is dextrorotatory, and the change is accompanied by a certain amount of racemisation, which is less pronounced when the temperature at which the displacement occurs is kept low. The behaviour of the *d*-hydroxy-acid towards hydrobromic acid is, of course, similar. Phosphorus pentabromide also brings about a change of sign of rotation by its action on the active hydroxy-acids. When the bromine in the active bromo-acids is displaced by the hydroxy-group, either by means of silver oxide and water, or by sodium carbonate and water or by water alone, a change of sign of rotation again occurs. The parent acid is accordingly regenerated:



The displacement of the hydroxy-group in the active β -hydroxy- β -phenylpropionic acids by the bromine atom appears to be a normal action, since both phosphorus pentabromide and hydrobromic acid act in a similar manner, and since a change of sign also accompanies the action of hydrobromic acid on the methyl *d* ester.

There is, therefore, no evidence of the occurrence of a Walden inversion in any of the changes studied.

EXPERIMENTAL.

Resolution of Inactive β -Hydroxy- β -phenylpropionic Acid.

Inactive β -hydroxy- β -phenylpropionic acid was prepared by the action of boiling water on inactive β -bromo- β -phenylpropionic acid, which is readily obtained from hydrobromic acid and cinnamic acid (Fittig and Binder, *Annalen*, 1879, 195, 131).

The resolution by means of morphine proceeds with exceptional ease. So far as we are able to judge, it is immaterial whether synthetic or storax cinnamic acid is used as the starting point for the preparation of the inactive acid.

Powdered morphine (61 grams) was added to a solution of 36 grams of the hydroxy-acid in 750 c.c. of boiling water. Crystallisation began after the solution was allowed to cool at the ordinary temperature for one hour; the solution was then stirred occasionally, and left overnight at the ordinary temperature. About half of the total morphine salt separated. The crystals, which melted and decomposed at about 206° were suspended in 50 c.c. of water and the morphine precipitated by means of a slight excess of ammonia. The addition of an excess of hydrochloric acid to the filtrate, from which the morphine

had been separated, caused the gradual separation, in the form of needles, of the *l*-acid, which is sparingly soluble in water. The acid was drained off and, after crystallisation from 300 c.c. of benzene, was pure. The yield amounted to 9 grams. Its melting point and its specific rotation did not alter after it had been recrystallised several times from benzene.

l- β -Hydroxy- β -phenylpropionic acid, $C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot CO_2H$, is sparingly soluble in water and in benzene. It separates in colourless needles and melts at 115–116°:

0.1925 gave 0.4579 CO_2 and 0.1032 H_2O . $C = 64.9$; $H = 6.0$.

$C_9H_{10}O_3$ requires $C = 65.0$; $H = 6.1$ per cent.

Its rotation was determined in ethyl-alcoholic solution:

$$l = 2, c = 5.153, \alpha_D^{20} - 1.95^\circ, [\alpha]_D^{20} - 18.9^\circ.$$

In order to obtain the enantiomorphously related isomeride, the mother liquor, from which the morphine *l*-salt had been separated, was concentrated by evaporation to 150 c.c., when no separation of salt took place. The dextro-acid was then separated in the manner described above and crystallised from benzene. The yield amounted to 10 grams.

d- β -Hydroxy- β -phenylpropionic acid melts at 115–116°, and resembles its *l*-isomeride in other particulars:

0.194 gave 0.4633 CO_2 and 0.1051 H_2O . $C = 64.9$; $H = 6.0$.

$C_9H_{10}O_3$ requires $C = 65.0$; $H = 6.1$ per cent.

A determination of its specific rotation in ethyl-alcoholic solution gave a value in agreement with that of the *l*-acid:

$$l = 2, c = 5.194, \alpha_D^{20} + 1.99^\circ, [\alpha]_D^{20} + 19.2^\circ.$$

Although the inactive acid had not been resolved previously, the active acids have been obtained by Barkow (*Inaug. Diss.*, Strasburg, 1906), working in Erlenmeyer's laboratory, in the course of an investigation dealing with the α -halogen- β -hydroxy- β -phenylpropionic acids. Barkow found that when *d*- α -bromo- β -hydroxy- β -phenylpropionic acid, $C_6H_5 \cdot CH(OH) \cdot CHBr \cdot CO_2H$, was reduced by sodium amalgam, it was converted into *d*- β -hydroxy- β -phenylpropionic acid with $[\alpha]_D + 19^\circ$ in ethyl-alcoholic solution.

Action of Hydrobromic Acid on the Active β -Hydroxy- β -phenylpropionic Acids.

Attempts to resolve inactive β -bromo- β -phenylpropionic acid into its optically active isomerides were not promising. The bases employed caused some decomposition of the bromo-acid into styrene. The active bromo-acids were accordingly obtained from the corresponding

hydroxy-acids, but they underwent partial racemisation in the process of their formation by this method.

The *l*-hydroxy-acid (2.5 grams) was covered with aqueous hydrobromic acid, which had previously been saturated at 0°. The hydroxy-acid dissolved, and the bromo-acid separated. After one hour, water was added, the sparingly soluble acid drained off, washed with water, and dried over soda-lime under diminished pressure. The product had $[\alpha]_D^{25} + 16.8^\circ$ for $c = 2.029$ in ethyl-alcoholic solution. It was a mixture of the *r*- and *d*-bromo-acids, since its melting point was indefinite and its rotation changed on crystallisation. The effect of crystallising three times from carbon tetrachloride was to give an acid mixture, which contained more of the inactive form than before, the value for its rotation in ethyl-alcoholic solution being $[\alpha]_D + 8.5^\circ$ for $c = 2.05$.

If the fuming hydrobromic acid is shaken with the *l*-hydroxy-acid for a few minutes only at the laboratory temperature, the racemisation is less pronounced. In one experiment, for example, the crude bromo-acid, obtained from the *l*-hydroxy-acid, was crystallised once from carbon tetrachloride, and then gave $[\alpha]_D + 20.6^\circ$ for $c = 2.204$ in ethyl-alcoholic solution.

When the *d*-hydroxy-acid was shaken with aqueous hydrobromic acid, saturated at 0°, for two or three minutes at 0°, the crude bromo-acid which separated had $[\alpha]_D - 23.9^\circ$ for $c = 2.974$ in ethyl-alcoholic solution.

Obviously, therefore, the amount of racemisation could be lessened by maintaining the temperature low during the action of the hydrobromic acid. Forty c.c. of aqueous hydrobromic acid (saturated at 0°) were accordingly cooled to -10° , and 8.5 grams of the *l*-hydroxy-acid added. The rapid solution of the hydroxy-acid was succeeded by the separation of a voluminous crop of the bromo-acid. After five minutes, the crystals were separated, washed with a little water, and dried. The product melted indefinitely at $126-133^\circ$, and had $[\alpha]_D + 32.2^\circ$ for $c = 2.125$ in ethyl-alcoholic solution. It was crystallised from 65 c.c. of chloroform, and the crop which separated (6 grams) had $[\alpha]_D + 21^\circ$. From the mother liquor, two successive crops were withdrawn, the second of which (1.1 gram) had $[\alpha]_D + 58.3$ for $c = 1.03$ in ethyl-alcoholic solution, whilst the residual mother liquor yielded 2 grams of acid with $[\alpha]_D + 96.2^\circ$ for $c = 1.107$ in ethyl-alcoholic solution. An estimation of bromine in the latter acid indicated the presence of cinnamic acid together with the bromo-acid.

The pure active bromo-acids have accordingly a value for their specific rotation higher than 96.2° , and appear to be more readily soluble in most solvents than the inactive isomeride. Further attempts to isolate them were not made, since the points of interest,

from the point of view of this investigation, could be established by aid of the partly-racemised acids.

The *d*-hydroxy-acid gave similar results to the above when it was treated with fuming hydrobromic acid at -10° .

Action of Phosphorus Pentabromide on the l-Hydroxy-acid.

The *l*-acid was dissolved in a mixture of chloroform and ether and acted on with an excess of phosphorus pentabromide, the temperature being maintained low. The bromo-acid, obtained after decomposition of the acid bromide with water, gave $[\alpha]_D +14.4^{\circ}$ for $c=2.39$ in ethyl-alcoholic solution.

Thus phosphorus pentabromide behaves like hydrobromic acid in causing a change of sign of rotation when it acts on the active hydroxy-acid. As is usually the case when a phosphorus halide acts on an active hydroxy-acid, the formation of the halogen acid is accompanied by partial racemisation.

Formation of l-Bromo-ester from d-Hydroxy-ester.

d- β -Hydroxy- β -phenylpropionic acid was converted into its methyl ester by the Fischer-Speier method. This ester, which had $[\alpha]_D +14.1^{\circ}$ for $c=4.717$ in ethyl-alcoholic solution, was added to an excess of fuming hydrobromic acid at -10° , and, after shaking for five minutes, the bromo-ester was separated. It was laevorotatory, giving $[\alpha]_D -28.5^{\circ}$ for $c=6.654$ in ethyl-alcoholic solution.

The action of phosphorus pentabromide on the *d*-hydroxy-ester was also examined, the bromination being effected in dry chloroform and at a low temperature. The resulting bromo-ester was again laevorotatory, giving $[\alpha]_D -4.6^{\circ}$ for $c=3.03$ in ethyl-alcoholic solution.

Displacement of Bromine in the d-Bromo-acid by the Hydroxy-group.

A mixture of the dextro- and inactive bromo-acids (0.4 gram) with $[\alpha]_D +58.3^{\circ}$ was added to water (10 c.c.), and, after five days at the ordinary temperature, the solution was heated for a few minutes until the odour of styrene had disappeared. The product was then evaporated to dryness at the ordinary temperature under diminished pressure. The residue gave the value $[\alpha]_D -7.7^{\circ}$ for $c=2.27$ in ethyl-alcoholic solution.

A mixture of the dextro- and inactive bromo-acids (0.7 gram) with $[\alpha]_D +58.3^{\circ}$ was added to a solution of 0.4 gram of sodium carbonate in 10 c.c. of water. After five days, the small amount of styrene present was removed. On acidification with hydrochloric acid, there

was no appreciable separation of cinnamic acid. The hydroxy-acid was extracted with ether, and had the specific rotation $[\alpha]_D - 5.5^\circ$ for $c = 1.451$ in ethyl-alcoholic solution.

Silver oxide, obtained from 1 gram of silver nitrate, was added to the dextrorotatory bromo-acid (0.7 gram) with $[\alpha]_D + 96.2^\circ$ and 10 c.c. of water. After twenty-four hours, with occasional shaking, the product was treated with hydrochloric acid, filtered, and the filtrate extracted with ether. The resulting hydroxy-acid gave the value $[\alpha]_D - 13.7^\circ$ with $c = 1.17$ in ethyl-alcoholic solution.

In these cases, therefore, using either water alone, sodium carbonate and water, or silver oxide and water, the hydroxy-acid recovered is opposite in sign to that of the bromo-acid used, and of the same sign as the parent hydroxy-acid from which the bromo-acid was obtained.

BIRKBECK COLLEGE,
LONDON, E.C.

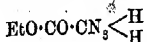
XV.—The Triazo-group. Part XI. Substituted Triazomalonic and Phenyltriazooacetic Acids.

By MARTIN ONSLOW FORSTER and ROBERT MÜLLER.

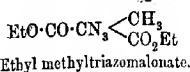
PURSuing our study of the effect produced by environment on the behaviour of the triazo-group, we deal in the present communication with substituted triazomalonic acids, for the purpose of comparison with the series of monobasic fatty acids already considered in previous papers (Trans., 1908, 93, 72; 1909, 95, 191). It has been shown that the characteristic manner in which triazoacetone is decomposed by alkalis may be deeply modified by exchanging the unsubstituted methyl group for ethoxyl, the azidic radicle in triazoacetic ester and its homologues being quite indifferent towards alkali, the attack of which is resisted even by the triazo-acids themselves unless considerable excess of the agent is employed and the temperature raised to 50° or more. From the fact that in the series quoted, α -triazoisobutyric acid escaped altogether, it was concluded that the limiting condition for elimination of two-thirds the azidic nitrogen from triazo-acids depends on the association of hydrogen with the carbon atom which carries the triazo-group.

Accepting ethyl triazoacetate as a standard, the series of substituted triazomalonic esters described in this paper may be regarded as derived by replacing one or both atoms of hydrogen with carboxyethyl,

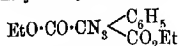
alkyl, phenyl, or triazidic groups, as represented by the following constitutional formulæ:



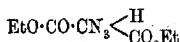
Ethyl triazacetate.



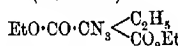
Ethyl methyltriazomalonate.



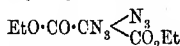
Ethyl phenyltriazomalonate.



Ethyl triazomalonate
(not isolated).



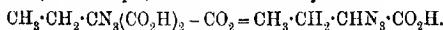
Ethyl ethyltriazomalonate.



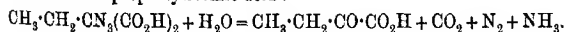
Ethylbistriazomalonate.

The first point to notice in connexion with the above series is that the introduction of a second carboxyethyl group into the molecule of triazacetic ester disturbs so profoundly the equilibrium of the molecule that ethyl triazomalonate is not capable of separate existence. All attempts to prepare this compound by variations of the original process for obtaining triazo-esters have been fruitless, not from want of reactivity between sodium azide and the halogen of the substituted malonate, but because under those circumstances in which double decomposition can be brought about, the product immediately undergoes profound decomposition, and gives rise to nitrogen, ammonia, and hydrazoic acid, along with a solid nitrogenous compound of high molecular weight. As soon as the remaining hydrogen atom is replaced, however, whether by alkyl, phenyl, or the triazo-group, stability returns to the molecule, and the substituted triazomalonate ester is sufficiently cohesive not only to withstand the action of alkali, but actually to undergo hydrolysis, furnishing the substituted triazomalonate acid.

In the alkyltriazomalonate acids we have to deal with substances directly comparable with α -triazoisobutyric acid, inasmuch as the triazotised carbon atom is tertiary. Accordingly they display unusual resistance towards alkali, which depends for the success of its attack on the well known power of substituted malonic acids to lose one molecule of carbon dioxide. Making this alteration in ethyltriazomalonate acid, for example, leads to α -triazobutyric acid:

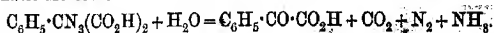


Consequent on this, there occurs elimination of two-thirds the azidic nitrogen, so that the net result of decomposing ethyltriazomalonate acid with alkali is propionylformic acid:

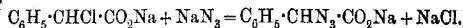


Proceeding now to consider the effect of the phenyl group, an increase in the reactivity of the molecule is to be noted, and although it has proved possible to hydrolyse the ester to phenyltriazomalonate

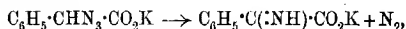
acid, and by the action of ammonia to prepare phenyltriazomalonic acid, nevertheless the further breakdown to benzoylformic acid is accomplished more readily than the corresponding degradation of the purely aliphatic molecule:



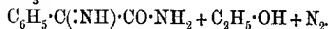
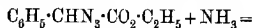
This access of reactivity is shown still more clearly by the behaviour of phenyltriazooacetic ester, which we have prepared for comparison with triazooacetic ester. Whilst the latter substance may be hydrolysed to the acid without risk of eliminating the two-thirds nitrogen, phenyltriazooacetic ester is so sensitive towards alkali that the acid cannot be prepared by hydrolysis, but must be derived from sodium phenylchloroacetate by double decomposition with sodium azide:



By proceeding carefully it is possible to arrest decomposition of phenyltriazooacetic acid with alkali at the stage intermediate between the original substance and benzoylformic acid, namely, potassium phenyliminoacetate:



but this compound readily suffers hydrolysis to potassium benzoylformate and ammonia. The instability of phenyltriazooacetic ester is illustrated still better by its behaviour towards ammonia, which converts it into phenyliminoacetamide with loss of two-thirds nitrogen and without formation of phenyltriazooacetamide.

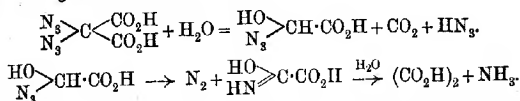


The latter substance, in fact, could not be isolated, although the transformation of triazooacetic ester into triazooacetamide by the direct action of ammonia is practically quantitative.

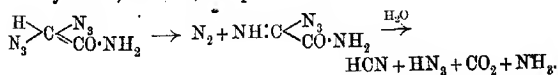
Proceeding now to the bistriazo-derivatives, we are confronted with another illustration of the comparative immunity of the triazo-group when the carbon atom which carries it is, tertiary. In studying the properties of bistriazoacetic ester (Trans., 1908, 93, 1073), it was found that potassium hydroxide readily eliminates hydrazoic acid, and that even ammonia brings about this change too rapidly to permit the production of bistriazoacetamide; moreover, during the preparation of the ester it was noticed that the double decomposition between dichloroacetic ester and sodium azide was accompanied by continuous liberation of hydrazoic and prussic acids, indicating subsidiary changes which reduced the yield very much below that required by theory. Bistriazomalonic ester, on the other hand, is a comparatively stable substance, and, although exploding with some violence at 180°, is much less dangerous to handle than bistriazoacetic ester. Ammonia converts

it into bistriazomalnamide, and although this change is accompanied by elimination of hydrazoic acid, the isolation of a solid amide represents a distinct superiority to the behaviour of the bistriazoacetic ester. As might be expected, however, the amide is much more sensitive towards concentrated sulphuric acid than methyltriazonmalonamide and ethyltriazonmalonamide, and is completely broken down by potassium hydroxide, yielding nitrogen and ammonia with prussic and hydrazoic acids.

An attempt to produce bistriazomalonic acid by cautious hydrolysis leads us to believe that this substance, like triazomalonic acid, is capable of existing in solution, but not in the individual state. An ethereal solution was concentrated without heating, but thereby acquired a powerful odour of hydrazoic acid, which remained noticeable during many days' exposure to reduced pressure; a few crystals of oxalic acid separated, and the oil, when quite free from hydrazoic acid, gave a nitrogen percentage agreeing fairly well with that of triazoglycollic acid, this indication being further confirmed by analysis of the barium salt. It appears probable, therefore, that bistriazomalonic acid undergoes the following changes in solution:



The production of prussic acid during the disruption of the triazogroup appears to be a feature of bistriazo-derivatives exclusively, and we have searched again for this compound among the products of decomposing with alkali those triazo-acids and triazo-esters which have been described in previous papers, with a negative result; it is, however, noteworthy that phenyltriazonmalonamide, when warmed with alkali, gives a distinct odour of phenylcarbylamine. It is difficult to explain the formation of prussic acid from bistriazomalonamide unless the production of the substance is preceded by the loss of carbon dioxide, which would lead to bistriazoacetamide; this might be expected to lose two-thirds the nitrogen of one azidic group, yielding a highly unstable molecule which would become resolved into ammonia with hydrazoic, carbonic, and prussic acids:



Such a change appears more probable when it is recalled that Conrad and Bruckner have shown that dichloroacetamide is among the products of treating dichloromalonic ester with ammonia (*Ber.*, 1891, 24, 2994).

Much remains to be learned, however, in connexion with those bistriazo-compounds in which both azidic groups are attached to the same carbon atom, other points in addition to those mentioned serving to emphasise the characteristic behaviour of such substances. Bistriazomalonic ester, for example, is remarkably stable, and does not appear to undergo alteration with lapse of time, whilst bistriazo-acetic ester develops the odour of prussic acid and deposits, in the course of a few months, massive, transparent crystals (m. p. 91°) containing more carbon, but less nitrogen, than the original material. This rearrangement will be investigated further, as there doubtless occurs some change comparable with the triazole formation which takes place in the molecule of allylazoimide (Trans., 1908, 93, 1174), and with the production of 1-hydroxy-5-phenyltetrazole from benz-hydroxamic chloride and sodium azide (Trans., 1909, 95, 183); the recent observation of Schroeter (*Ber.*, 1909, 42, 2336), who obtained diphenyltetrazole from diphenylbistriazomethane, belongs, probably, to the same class of transformation.

EXPERIMENTAL.

Interaction of Chloromalonic Ester and Sodium Azide.

Fifty grams of chloromalonic ester (b. p. 91°/2 mm.) were heated under reflux on the water-bath with 25 grams of alcohol, 20 grams of sodium azide, and sufficient water to maintain the salt in solution; the mixture rapidly became yellow, then dark red, while brisk effervescence was set up, the escaping gases being nitrogen, ammonia, and hydrazoic acid. After four hours the liquid was allowed to cool, and filtered from 3 grams of crystalline material, of which a further quantity about equal to the first was obtained by removing esters in a current of steam, concentrating the residue to about 200 c.c., and then adding dilute sulphuric acid. The substance was purified by precipitation with sulphuric acid from the solution in sodium carbonate, followed by successive recrystallisation from boiling alcohol and ethyl acetate independently, approximately one litre of the latter solvent being required by 0.5 gram; it crystallised in minute, colourless needles, became deep red at about 220°, and decomposed completely in the neighbourhood of 240°. Many analyses have been made, of which the following are typical, without, however, revealing the identity of this compound, but they point consistently to a molecule arising by condensation of two or more molecules of triazomalonic ester:

0.2061 gave 0.3577 CO₂ and 0.0908 H₂O. C = 47.29; H = 4.90.

0.1181 „ 13.2 c.c. N₂ at 20° and 746.5 mm. N = 12.56.

(C₉H₁₁O₃N₂)_x requires C = 47.58; H = 4.84; N = 12.33 per cent.

The substance is very sparingly soluble in boiling water, alcohol, chloroform, and ethyl acetate; it does not reduce ammoniacal silver oxide, and does not give any characteristic coloration when ferrous sulphate is added to a very dilute solution in sodium hydroxide, but a solution in cold absolute alcohol, which of necessity contains only a minute portion of the substance, develops an intense violet coloration with ferric chloride.

As regards the preparation of triazomalonic ester, the foregoing experiment was a failure, because not only is the solid product quite distinct from a triazo-compound, but the volatile oil removed by steam was found not to contain nitrogen. Another fruitless attempt to obtain the substance consisted in shaking during twenty hours at laboratory temperature a suspension of chloromalonic ester (50 grams) in aqueous alcohol containing sodium azide (20 grams); the mixture became dark red, and pressure was developed, but the odour of ammonia or hydrazoic acid was not perceptible, and the heavy oil which remained undissolved consisted of original material.

Having found that sodium phenyltriazooacetate may be prepared from the chloro-compound by the action of aqueous sodium azide, 35 grams of bromomalonic acid were neutralised with sodium carbonate, and gently warmed with 10 grams of sodium azide dissolved in water. It soon became evident that double decomposition had occurred, because a test with 40 per cent. potassium hydroxide gave torrents of nitrogen and ammonia, but on extracting the acidified solution with ether, and evaporating the solvent under reduced pressure, hydrazoic acid was liberated continuously, leaving an oil which no longer evolved nitrogen when treated with alkali.

Methyltriazomalonic Acid, $\text{CH}_3\cdot\text{CN}_3(\text{CO}_2\text{H})_2$.

Five grams of methyltriazomalonic ester were shaken with 5 grams of potassium hydroxide dissolved in 5 c.c. of water until, after about twenty minutes, the oil had disappeared, when the liquid was gradually acidified with 50 per cent. sulphuric acid and extracted with ether. The residue from the latter solidified in the desiccator, and, after crystallisation from warm benzene, was redissolved in its own weight of ethyl acetate; on adding benzene in approximately equal volume, there separated stellate aggregates of long, transparent prisms melting at 87.5° :

0.1551 gave 37.0 c.c. N_2 at 23° and 743 mm. $N = 26.40$.

$\text{C}_4\text{H}_5\text{O}_4\text{N}_3$ requires $N = 26.41$ per cent.

The acid is very hygroscopic, and dissolves freely in ethyl acetate; benzene dissolves it only sparingly, however, and it is insoluble in petroleum. Concentrated sulphuric acid attacks the substance

very slowly, whilst stannous chloride in hydrochloric acid liberates nitrogen immediately.

The silver salt was precipitated by silver nitrate from aqueous ammonium methyltriazomalonate, and, although colourless when fresh, rapidly darkened on attempting to recrystallise it from warm water; a small quantity of the dried substance detonated with considerable violence when thrown on a hot plate.

Ethyl Methyltriazomalonate, $\text{CH}_3\cdot\text{CN}_3(\text{CO}_2\cdot\text{C}_2\text{H}_5)_2$.

Fifty grams of methylbromomalononic ester in 30 c.c. of absolute alcohol were heated under reflux during ten hours with 22 grams of sodium azide in 30 c.c. of water; action being then complete, a considerable quantity of water was added, and the precipitated oil distilled under diminished pressure, the principal fraction (32 grams) boiling at $69^\circ/0.6$ mm.:

0.1328 gave 23.0 c.c. N_2 at 17° and 749 mm. $\text{N} = 19.80$.

$\text{C}_8\text{H}_{13}\text{O}_4\text{N}_3$ requires $\text{N} = 19.53$ per cent.

Ethyl methyltriazomalonate is a colourless liquid having sp. gr. 1.11695 at $16^\circ/16^\circ$; it has a faint, agreeable perfume, suggesting acetoacetic ester, and the vapour when inhaled with steam produces an effect on the blood-pressure similar to that of the esters in the monobasic series. As already indicated, cold concentrated potassium hydroxide merely hydrolyses the ester, provided that the alkali is not in great excess and the mixture is not heated; even on evaporating to dryness, the liberation of gas is very slight, and only a small proportion of nitrogen is removed in the form of hydrazoic acid.

Action of Sulphuric Acid.—As in the case of triazoacetic ester, the interaction with concentrated sulphuric acid is very slow, and only on heating the mixture during a considerable period did the volume of liberated nitrogen reach the calculated amount:

0.2243 gave 26.8 c.c. N_2 at 17° and 747 mm. $\text{N} = 13.62$.

$\text{C}_8\text{H}_{12}\text{O}_4\text{N}_3$ requires $2/3\text{N} = 13.02$ per cent.

Behaviour towards Stannous Chloride.—A solution of stannous chloride in hydrochloric acid is without action on the ester until the temperature reaches about 80° , when a slow but regular effervescence sets in, and is completed in about two hours.

0.3038 gave 36.6 c.c. N_2 at 19° and 742 mm. $\text{N} = 13.51$.

$\text{C}_8\text{H}_{12}\text{O}_4\text{N}_3$ requires $2/3\text{N} = 13.02$ per cent.

Methyltriazomalonomide, $\text{CH}_3\cdot\text{CN}_3(\text{CO}\cdot\text{NH}_2)_2$.

Five grams of the ester were shaken during two hours with 15 c.c. of concentrated aqueous ammonia, excess of which was removed in the vacuum desiccator after twelve hours had elapsed. The crystalline amide was dissolved in boiling benzene, of which about 400 c.c. were required per gram, separating in long, lustrous needles melting at 137.5° :

0.1330 gave 52.5 c.c. N_2 at 17° and 742 mm. $\text{N} = 44.71$.

$\text{C}_6\text{H}_7\text{O}_2\text{N}_3$ requires $\text{N} = 44.58$ per cent.

Methyltriazomalonomide is readily soluble in warm water, alcohol, and petroleum, but is insoluble in cold benzene. A hydrochloric acid solution of stannous chloride attacks the substance rapidly without being heated, and liberates nitrogen. Concentrated sulphuric acid behaves in a most unusual manner, nitrogen being evolved only slowly even on raising the temperature to 125° , below which there is not any effervescence. A parallel with this remarkable behaviour has been noted quite recently in the case of triphenylmethylazoisimide (Wieland, *Ber.*, 1909, 42, 3027), the solution of which in concentrated sulphuric acid must be heated to 200° before gas evolution becomes vigorous.

Ethyltriazomalonic Acid, $\text{C}_2\text{H}_5\cdot\text{CN}_3(\text{CO}_2\text{H})_2$.

Exactly the same procedure was adopted as in the case of methyltriazomalonic acid, and, after crystallisation from hot benzene, the acid was obtained in colourless, rhombic, hygroscopic prisms, melting and decomposing at $105-107^\circ$:

0.1632 gave 34.4 c.c. N_2 at 22° and 766 mm. $\text{N} = 24.12$.

$\text{C}_6\text{H}_7\text{O}_4\text{N}_3$ requires $\text{N} = 24.28$ per cent.

The acid is attacked readily by concentrated sulphuric acid, and by stannous chloride in hydrochloric acid.

Ethyl Ethyltriazomalonate, $\text{C}_2\text{H}_5\cdot\text{CN}_3(\text{CO}_2\cdot\text{C}_2\text{H}_5)_2$.

The ester was prepared from 42 grams of ethylbromomalonic ester, 15 grams of sodium azide, and 45 c.c. of 50 per cent. alcohol, heating under reflux being continued during eight hours; the product was fractionated under reduced pressure, boiling at $83.5^\circ/0.7$ mm.:

0.1670 gave 27.3 c.c. N_2 at 22° and 769 mm. $\text{N} = 18.74$.

$\text{C}_{10}\text{H}_{15}\text{O}_4\text{N}_3$ requires $\text{N} = 18.38$ per cent.

The colourless liquid has sp. gr. 1.1161 at $16^\circ/16^\circ$, and the vapour,

although characterised by a pleasant odour, has the disagreeable effect on the blood-pressure which has become associated with the aliphatic triazo-esters. Whilst the effervescence brought about by stannous chloride in hydrochloric acid is very vigorous, that induced by concentrated sulphuric acid is very slow. A distinction from the lower homologues is offered by the behaviour towards concentrated potassium hydroxide, because on heating the ester with excess of this agent, violent liberation of nitrogen sets in, followed by ammonia, and, on cooling the liquid, there separate crystals of potassium propionyl-formate, containing 28.2 per cent. of potassium ($C_4H_5O_2K$ requires $K = 27.9$ per cent.); the phenylhydrazone was prepared, and melted at 148.5° after crystallisation from dilute alcohol.

Ethyltriazomalonamide, $C_5H_5 \cdot CN_3(CO \cdot NH_2)_2$

The substance was obtained by shaking the ester with concentrated aqueous ammonia, and crystallised from hot benzene in colourless, rhombic plates melting at 167° :

0.1027 gave 36.8 c.c. N_2 at 20° and 763 mm. $N = 41.05$.

$C_5H_5O_2N_5$ requires $N = 40.93$ per cent.

Decomposition with stannous chloride in hydrochloric acid readily gave the calculated amount of nitrogen, but the remarkable behaviour of the lower homologue towards concentrated sulphuric acid was reproduced by ethyltriazomalonamide, which was not decomposed below 125° .

Phenyltriazomalononic Acid, $C_6H_5 \cdot CN_3(CO_2H)_2$

As appears below, it was not found possible to distil phenyltriazomalononic ester, even under pressure reduced to 0.56 mm., without decomposition, which took place at 150° , and accordingly the undistilled material was employed as the source of the acid. Several grams of the ester were shaken with the calculated amount of potassium hydroxide in the form of a 20 per cent. aqueous solution until, in the course of about three hours, a clear liquid resulted; this was extracted twice with ether, acidified with the calculated amount of dilute sulphuric acid, saturated with solid ammonium sulphate, and further extracted five times with ether. After drying with ignited sodium sulphate, the residue from evaporation was submitted to diminished pressure (20 mm.) during thirty-four hours, when it solidified and became colourless on porous earthenware. Recrystallisation from hot benzene gave spherical clusters of snow-white needles melting at 99° without decomposition:

0.1562 gave 25.8 c.c. N_2 at 18° and 768 mm. $N = 19.28$.

$C_9H_7O_4N_5$ requires $N = 19.00$ per cent.

Phenyltriazomalonie acid effervesces vigorously with concentrated sulphuric acid, while torrents of nitrogen are liberated by a solution of stannous chloride in hydrochloric acid; 40 per cent. aqueous potassium hydroxide effects immediate disruption of the triazo-group in the cold, but alkali of half this concentration requires to be heated before bringing about decomposition, when ammonia and nitrogen are liberated without formation of hydrazoic and hydrocyanic acids. The alkaline liquid from the foregoing experiment gave an immediate precipitate with phenylhydrazine after being neutralised with dilute sulphuric acid; this was found to be identical with the phenylhydrazone of benzoylformic acid obtained by similar procedure from phenyltriazooacetic acid, whence it follows that the disruption of the triazo-group is preceded by removal of carbon dioxide from the dibasic acid.

Ethyl Phenyltriazomalonate, $C_6H_5 \cdot CN_3(CO_2 \cdot C_2H_5)_2$

Phenylmalonic ethyl ester was prepared according to the method of Wislicenus (*Ber.*, 1894, 27, 1093; *Annalen*, 1888, 246, 315), which depends on elimination of carbon monoxide from phenyloxalic ester obtained by the action of ethyl oxalate on the sodium derivative of ethyl phenylacetate. Wislicenus states that ethyl phenylmalonate tends to decompose when boiled under atmospheric pressure at 285°, and therefore distilled it at 170—172°/14 mm.; our specimen boiled at 127—129°/0.35—0.4 mm. The bromination of phenylmalonic ester has been described by Wheeler and Johnson (*J. Amer. Chem. Soc.*, 1902, 24, 680), who carried out this operation in sealed tubes, but we find that phenylbromomalonie ester may be prepared in almost quantitative yield by heating the ester with the halogen under ordinary pressure at 140—150° in bright daylight, the product distilling at 141—142°/0.48 mm.

Phenylbromomalonie ester (18.5 grams), sodium azide (6 grams), and alcohol (10 c.c.), with sufficient water to maintain the salt dissolved, were left in darkness during three weeks with frequent shaking and occasional warming to about 40°; water was then added, and the precipitated ester extracted and dried, but an attempt to distil the product was fruitless, owing to the decomposition which was threatened on raising the temperature of the bath to 150°, when the pressure rose from 0.56 mm. to 1.5 mm. quite suddenly, and the operation was therefore discontinued. There was not any indication of distillation taking place, and it has not been possible, therefore, to obtain the substance in purified condition.

The crude ester is a slightly yellow, heavy oil with a faint, pleasant perfume; the decomposition with concentrated sulphuric acid takes

place readily, and nitrogen is liberated also by a solution of stannous chloride in hydrochloric acid. The action of potassium hydroxide has been already described.

Phenyltriazomalonamide, $C_6H_5 \cdot CN_3(CO \cdot NH_2)_2$.

On continued shaking with strong aqueous ammonia, phenyltriazomalonamic ester was transformed into a crystalline solid, which dissolved in hot water, and separated therefrom in snow-white, fern-like leaflets; the substance melted at 189° :

0.1038 gave 29.7 c.c. N_2 at 23° and 760 mm. $N = 32.24$.

$C_9H_5O_2N_5$ requires $N = 31.96$ per cent.

Phenyltriazomalonamide is moderately soluble in acetone, ethyl acetate, and ethyl alcohol; it dissolves sparingly in boiling benzene, and is insoluble in boiling petroleum.

The action of concentrated sulphuric acid on the amide is mild at first, and becomes brisk only on continued stirring, whilst a solution of stannous chloride in hydrochloric acid does not liberate nitrogen until a few drops of alcohol have been added to complete contact. When heated with 20 per cent. aqueous potassium hydroxide, the compound evolves nitrogen freely, accompanied by ammonia, the odour of phenylcarbamylamine being also noticeable; hydrazoic and prussic acids, however, were not produced.

Ethyl Bistriazomalonate, $(N_3)_2C(CO_2 \cdot C_2H_5)_2$.

Ethyl dichloromalonate was obtained as a by-product in the preparation of ethyl chloromalonate on treating malonic ester with chlorine at 80° , and boiled at $231-234^\circ$. It is noteworthy that, although ethyl dichloromalonate may be preserved during many months without showing any signs of having undergone change, the monochloro-compound (b. p. $222-223^\circ$) became transformed into a brownish-grey, fuming liquid, having a marked odour of hydrogen chloride.

Twenty grams of rectified dichloromalonate ester, 20 c.c. of absolute alcohol, and 14 grams of sodium azide dissolved in 40 c.c. of water were warmed carefully until the liquid became clear, and left in darkness during one month, with occasional shaking and gentle warming. On diluting with water and extracting with ether, a colourless oil was obtained, half a gram of which was heated in an open tube under atmospheric pressure before submitting the whole specimen to distillation; no change was observed to take place while the temperature remained below 245° , but at the moment of reaching 180° an explosion of very considerable violence occurred. The main quantity of ester

was then distilled under 0.81 mm. pressure, boiling steadily at 115–116.5°.

0.1576 gave 47.6 c.c. N_2 at 21° and 764 mm. $N = 34.57$.

$C_7H_{10}O_4N_4$ requires $N = 34.71$ per cent.

Bistriazomalonic ester is a colourless oil with a pleasant perfume; it has sp. gr. 1.2136 at 20° compared with water at the same temperature. The decomposition by concentrated sulphuric acid is extremely violent, and the liberation of nitrogen with stannous chloride in hydrochloric acid torrential:

0.3251 gave with $SnCl_2$ 62.6 c.c. N_2 at 21° and 768 mm. $N = 22.3$.

0.1816 „ „ H_2SO_4 36.2 c.c. N_2 „ 21° „ 764 mm. $N = 22.8$.

$C_7H_{10}O_4N_4$ requires $2/3N = 23.14$ per cent.

An attempt to prepare bistriazomalonic acid by hydrolysing the ester with 10 per cent. alkali was unsuccessful, owing to the readiness with which the product undergoes spontaneous loss of hydrazoic acid. Seven grams were shaken with the calculated amount of the agent until dissolved, extracted with ether, and treated with the exact quantity of dilute sulphuric acid, after which ammonium sulphate was added and the bistriazomalonic acid removed by four extractions with ether. The solvent having been evaporated without heating, it was noticed that the residual oil, which remained viscous, acquired a distinct odour of hydrazoic acid, and was filled with bubbles which ceased to appear after many days in the desiccator:

0.1410 gave 43.4 c.c. N_2 at 23° and 757 mm. $N = 34.6$.

$C_5H_2O_4N_6$ requires $N = 45.16$ per cent.

$C_2H_3O_3N_3$ „ $N = 35.8$ „

The latter formula represents triazoglycollic acid, which is very likely produced by the removal of carbon dioxide and hydrazoic acid from bistriazomalonic acid under the influence of water. After many days, crystals of oxalic acid were noticed in the oil, which was treated with a paste of barium carbonate in order to isolate, if possible, barium triazoglycollate. The aqueous filtrate from barium oxalate and unchanged barium carbonate was evaporated to dryness without heat, and triturated with absolute alcohol, the insoluble portion being then analysed:

0.0786 gave 0.0498 $BaSO_4$. $Ba = 37.25$.

$C_4H_4O_6N_6$ Ba requires $Ba = 37.13$ per cent.

The substance effervesced vigorously with concentrated sulphuric acid, and was most probably barium triazoglycollate.

Bistriazomalonamide, (N₃)₂C(CO·NH₂)₂

Agitation with strong aqueous ammonia during one hour transformed bistriazomalononic ester into a snow-white, crystalline solid, which was recrystallised from boiling water, being only very sparingly soluble therein; the amide separated in transparent, colourless prisms, melting at 162° with vigorous decomposition:

0.0866 gave 47.6 c.c. N₂ at 24° and 765 mm. N = 60.88.

C₃H₄O₂N₃ requires N = 60.89 per cent.

The substance is readily soluble in hot acetone and ethyl acetate, crystallising therefrom in six-sided plates; it is moderately soluble in cold alcohol, but dissolves very sparingly in boiling benzene and in boiling chloroform. Immediate effervescence occurs on mixing the amide with concentrated sulphuric acid, and becomes very vigorous on warming; stannous chloride also liberates nitrogen very freely. The decomposition with 40 per cent. potassium hydroxide is most profound, giving rise to nitrogen, ammonia, prussic acid, and hydrazoic acid.

Phenyltriazooacetic Acid, C₆H₅·CHN₃·CO₂H.

Owing to the readiness with which the triazo-group in phenyltriazooacetic ester undergoes disruption in the presence of alkali, the acid cannot be obtained by hydrolysis. Five grams of phenylchloroacetic acid were therefore exactly neutralised with sodium carbonate in about 30 c.c. of water, and, after admixture with 2.5 grams of sodium azide dissolved in 20 c.c. of water, allowed to remain during two days protected from light; dilute sulphuric acid having been added, and the liquid extracted six times with ether, the latter was dried with sodium sulphate and evaporated in a vacuum desiccator without being heated. The residue became solid, and was recrystallised three times from benzene, which deposited the substance in thin, colourless, rhombic plates melting at 98.5°:

0.1543 gave 31.4 c.c. N₂ at 20° and 764 mm. N = 23.41.

C₆H₇O₂N₃ requires N = 23.73 per cent.

The decomposition with concentrated sulphuric acid was very violent, and nitrogen was also liberated immediately on mixing the acid with aqueous potassium hydroxide or a solution of stannous chloride in hydrochloric acid. The silver salt could not be analysed, because reduction took place on attempting to recrystallise it from warm water.

Ethyl Phenyltriazooacetate, C₆H₅·CHN₃·CO₂·C₂H₅.

Early attempts to prepare this ester were conducted on the lines followed in the case of triazooacetic ester and its higher homologues,

but the results were unsatisfactory; when alcoholic phenylchloroacetic ester is heated under reflux with aqueous sodium azide, the liquid rapidly becomes yellow and evolves gas, and, although the oily product of steam distillation answers to the azide test with concentrated sulphuric acid, it is too complex a mixture to repay further treatment, the presence of by-products being best avoided by the following procedure.

Eighty grams of phenylchloroacetic ester (b. p. 135°/17 mm.) were mixed with 100 grams of alcohol and 40 grams of sodium azide (1 mol. = 26.2 grams), water and alcohol being then added alternately until both ester and salt were dissolved; after remaining a few weeks in the dark, the liquid was found to have deposited a crop of sodium chloride, and at the end of two months, when the action was judged to have been complete, water and solid ammonium sulphate were added to precipitate the ester, which was then removed, dried in the usual way, and fractionated with the aid of the Gaede pump:

0.2204 gave 38.3 c.c. N_2 at 16° and 770 mm. $N = 20.08$.

$C_{10}H_{11}O_2N_3$ requires $N = 20.49$ per cent.

Ethyl phenyltriazooacetate is a colourless liquid with a very faint pleasant perfume suggesting roses; only on distilling the ester with steam does the vapour produce the throbbing sensation at the base of the forehead and palpitation of the heart characteristic of the aliphatic triazo-esters. It boils at 93°/0.09 mm., and has sp. gr. 1.1434 at 20°/20°; the action with concentrated sulphuric acid is very violent.

Action of Potassium Hydroxide.—Contact with dilute aqueous alkali was found to bring about an immediate disruption of the triazo-group, and it was therefore useless to attempt hydrolysis by this means. On adding 40 per cent. potassium hydroxide drop by drop to 10 grams of the ester dissolved in 40 c.c. of alcohol, the liberation of nitrogen was perfectly regular, and, after excess of alkali had been added, there separated a reddish oil which in the vacuum-desiccator rapidly solidified; this product, being sparingly soluble in water, was recrystallised from the gently warmed liquid, and was obtained in colourless, nacreous plates:

0.3114 gave 0.1470 K_2SO_4 . $K = 21.16$.

0.2577 „ 16.7 c.c. N_2 at 19° and 768 mm. $N = 7.53$.

$C_8H_6O_2NK$ requires $K = 20.85$; $N = 7.49$ per cent.

In the course of twenty-four hours' exposure to air, the substance had begun to undergo hydrolysis, yielding potassium benzoylformate, and when the salt no longer contained nitrogen, benzoylformic acid was obtained from it and identified by the melting point (65°) and by conversion into the phenylhydrazone, a specimen of which melted at

160° and contained 11·8 per cent. of nitrogen ($C_8H_7O_2N_3$ requires $N=11·7$ per cent.).

Action of Ammonia.—Attempts to prepare phenyltriazacetamide by the action of ammonia on phenyltriazacetic ester were unsuccessful, owing to disruption of the triazo-group; this can, however, be so controlled as to permit the isolation of *phenyliminoacetamide*. Excess of dry ammonia was passed into a well-cooled solution of phenyltriazacetic ester in absolute alcohol; liberation of nitrogen accompanied the separation of crystals, which increased during twenty-four hours in the ice-chest. Recrystallisation from benzene, repeated until the melting point was constant, gave colourless, monoclinic plates melting at 144°:

0·2070 gave 34·3 c.c. N_2 at 20° and 770 mm. $N=19·21$.

$C_8H_7ON_3$ requires $N=18·92$ per cent.

The substance is readily soluble in alcohol and in benzene, being precipitated from the respective solutions by water and by petroleum. When exposed to air it produces ammonia, giving the α -amide of benzoylformic acid, m. p. 90°. The acid itself was obtained by completing the hydrolysis.

Triazacetophenone (Phenacylazoimide), $N_3 \cdot CH_2 \cdot CO \cdot C_6H_5$.

Twenty grams of bromoacetophenone dissolved in 50 c.c. of absolute alcohol and mixed with 7 grams of sodium azide in the minimum quantity of water were shaken at intervals during sixteen hours in the ice-chest; being very readily fusible, the crystalline product was collected on a filter, cooled with chilled brine, and then precipitated by petroleum from a dried ethereal solution:

0·1695 gave 38·4 c.c. N_2 at 20° and 767 mm. $N=26·16$.

$C_8H_7ON_3$ requires $N=26·09$ per cent.

The triazoketone crystallises in colourless, lustrous plates, and melts at 17°; in the course of a few weeks the pale yellow substance became dark brown, even when protected from light, and the odour of hydrazoic acid was perceptible. An attempt to distil it under 0·1 mm. pressure was unsuccessful, because a threatening decomposition set in when the temperature of the bath had reached 130°, the pressure quickly rising to 4 mm.

On adding 20 per cent. potassium hydroxide to an alcoholic solution of triazacetophenone, immediate liberation of nitrogen takes place followed by ammonia on heating the liquid; a deep red coloration is developed, but the indication of hydrazoic acid is trifling. An attempt to establish the intermediate production of benzoylformaldehyde on the lines indicated by W. L. Evans (*J. Amer. Chem. Soc.*, 1906, 34, 115) was unsuccessful, the only material isolated being

benzoic acid. Two grams in ether were shaken with one gram of lime and 40 c.c. of water, the mixture liberating gas immediately and becoming dark brownish-red; after thirty hours the aqueous liquid was removed, extracted three times with ether, and acidified, when further extraction removed benzoic, not mandelic, acid.

Phenacylazoimide reduces ammoniacal silver oxide in the cold solution.

Action of Sulphuric Acid.—The concentrated agent attacks the triazoketone with great violence, and flame sometimes accompanies the small explosion which occurs when they are mixed drop by drop. By using more dilute acid the action can be moderated, until at 25 per cent. the yield of nitrogen may be measured:

0.2336 gave 34.4 c.c. N_2 at 18° and 772 mm. $N = 17.27$.

$C_8H_7ON_3$ requires $2/3N = 17.39$ per cent.

To complete the decomposition it was found necessary to use a bath of hot brine, and on cooling the contents of the flask, crystals of benzoic acid separated.

Behaviour towards Stannous Chloride.—With a cold 20 per cent. solution of the metal in hydrochloric acid the decomposition was very slow, and, even after heating during two hours, the quantity of gas was deficient:

0.1586 gave 22.9 c.c. N_2 at 18° and 772 mm. $N = 16.95$.

$C_8H_7ON_3$ requires $2/3N = 17.39$ per cent.

The aromatic product was not identified.

The Semicarbazone.—An alcoholic solution of the triazoketone was mixed with aqueous semicarbazide acetate, the solid which separated during twelve hours being recrystallised from warm dilute alcohol:

0.0895 gave 29.6 c.c. N_2 at 19° and 773 mm. $N = 38.68$.

$C_8H_{10}ON_4$ requires $N = 38.52$ per cent.

The substance crystallised in colourless, silky needles, melting at 127.5 — 128.5° . The reaction with concentrated sulphuric acid was very vigorous.

The Bromophenylhydrazone.—The derivative crystallised from dilute alcohol in lustrous, yellow needles, melting at 114.5° :

0.1079 gave 20.1 c.c. N_2 at 19° and 768 mm. $N = 21.64$.

$C_{14}H_{12}N_3Br$ requires $N = 21.21$ per cent.

Triazoacetophenoneoxime, $N_3 \cdot CH_2 \cdot C(\cdot NOH) \cdot C_6H_5$.

Triazoacetophenone was suspended in an aqueous solution of hydroxylamine prepared by exactly neutralising with sodium carbonate a slight excess of the hydrochloride; alcohol was then added until, with gentle warming, a clear solution was produced. After three

days in the dark, a pale yellow oil had separated, and this, after adding water, was extracted with ether, dried with sodium sulphate, and freed from solvent in the vacuum desiccator. As in the case of triazacetone (Trans., 1908, 93, 84), it was not found possible to crystallise the oxime, which was therefore analysed in liquid form:

0.1050 gave 28.4 c.c. N_2 at 18° and 771 mm. $N = 31.70$.

$C_8H_8ON_4$ requires $N = 31.82$ per cent.

An attempt to produce the *p*-toluenesulphonyl derivative, which served to characterise triazacetoxime (*loc. cit.*), led to an uninviting black tar.

ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S.W.

XVI.—Organic Derivatives of Silicon. Part XII.* *Dibenzylethylpropylsilicane and Sulphonic Acids Derived from It.*

By FREDERICK CHALLENGER, B.Sc., and FREDERIC STANLEY KIPPING.

WHEN the study of organic derivatives of silicon was commenced by one of us, the principal object in view was the preparation of an optically active compound containing *one* asymmetric silicon group.

After a short experience of the behaviour of silicon derivatives, the plan which seemed to offer the best prospect of success was to synthesise some asymmetric silico-hydrocarbon, $SiR_1R_2R_3R_4$, which could afterwards be sulphonated, and then to resolve the *dl*-sulphonic acid which would be thus obtained.

In pursuance of this plan, phenylmethylethylpropylsilicane, $SiPhMeEtPr$, and phenylbenzylethylpropylsilicane, $SiPhEtPr \cdot CH_2Ph$, were first prepared; but on attempting to sulphonate these compounds, the phenyl group was eliminated as benzene and tertiary silicols were formed (Kipping, Trans., 1907, 91, 221).

In the case of the phenylbenzyl derivative, this unexpected behaviour did not necessitate any change in the original scheme, as it was found that a sulphonic acid could be obtained from the benzylethylpropylsilicol, $CH_2Ph \cdot SiEtPr \cdot OH$, which was produced from the silico-hydrocarbon.

Further investigation showed, however, that this sulphonic acid was derived from the oxide, $(SiEtPr \cdot CH_2Ph)_2O$, and therefore contained *two* asymmetric silicon groups; this fact, of course, upset the original

* Parts X and XI, Trans., 1909, 95, 302 and 489 respectively.

plan, but at the same time opened out an alternative one, for if the *dl*-sulphonic derivative of benzylethylpropylsilicyl oxide which was thus obtained proved to be the *dl*- and not the internally compensated compound, it might be resolved into its optically active components. These possibilities were ultimately realised, and in later investigations the resolution of the homologous sulphonic acid derived from benzylethylisobutylsilicyl oxide, $(C_4H_9 \cdot SiEt \cdot CH_2Ph)_2O$, was also accomplished (Kipping, *Trans.*, 1907, 91, 234; Luff and Kipping, *Trans.*, 1908, 93, 2090).

These acids, which owe their optical activity to the presence of *two* asymmetric silicon groups, are the only active silicon compounds which so far have been described; they hold this position, not because the original object has been abandoned, but because all attempts to attain it resulted in failure.

Thus, during the progress of the experiments referred to above, two other asymmetric silico-hydrocarbons, namely, benzylmethylethylpropylsilicane, $SiMeEtPr \cdot CH_2Ph$, and benzylethylpropylisobutylsilicane, $C_4H_9 \cdot SiEtPr \cdot CH_2Ph$ (Kipping, *Trans.*, 1907, 91, 717; Kipping and Davies, *Trans.*, 1909, 95, 69), were prepared and sulphonated, and many attempts were made to resolve the *dl*-acids thus produced. Although, however, the externally compensated character of the acids could hardly be open to question, no definite evidence of their asymmetry was obtained on fractionally crystallising their salts with active bases.

Our knowledge of asymmetric substances is still so incomplete that a reason for these repeated failures can hardly be suggested with any confidence. It seemed possible, however, that by preparing a compound in which the groups combined with the silicon atom were more widely different than those in the two acids under discussion, the chances of being able to accomplish a resolution would be increased.

Now as most of the readily available alkyl and aryl halogen compounds had already been utilised in the preparation of the four asymmetric silico-hydrocarbons referred to above, the simplest way of obtaining a new asymmetric sulphonic acid of the desired character seemed to be to prepare a silico-hydrocarbon containing two benzyl groups and two different alkyl groups, and then to convert this compound into an asymmetric acid by sulphonating one of the benzyl groups.

The present paper contains a record of the experiments which have led to the production of such an acid, namely, dibenzylethylpropylsilicanemonosulphonic acid, $CH_2Ph \cdot SiEtPr \cdot CH_2 \cdot C_6H_4 \cdot SO_3H$; the disulphonic acid, $SiEtPr(CH_2 \cdot C_6H_4 \cdot SO_3H)_2$, derived from the same silico-hydrocarbon has also been obtained.

Dibenzylethylpropylsilicane, $SiEtPr(CH_2Ph)_2$, was prepared by the

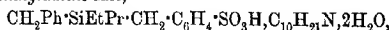
interaction of benzylethylpropylsiliclyl chloride (Kipping, Trans., 1907, 91, 722) and magnesium benzyl chloride; a simpler method, which was afterwards adopted, consisted in preparing dibenzylethylsiliclyl chloride directly from ethylsilicon trichloride and then treating this product with magnesium propyl bromide.

The compound thus obtained, like all those silico-hydrocarbons which contain a benzyl group, is readily attacked by chlorosulphonic acid at the ordinary temperature, and under suitable conditions it yields a monosulphonic acid, which, however, is invariably accompanied by a disulphonic acid. It would seem that in both cases only one of the possible structural isomerides is formed in appreciable quantities, namely, the para-derivative.

The isolation of these two sulphonic acids was by no means a simple task, but it was at last accomplished by two methods, namely, by fractionally crystallising the mixture of strychnine salts, or of *l*-menthylamine salts, prepared from the product of sulphonation. The disulphonic acid, which has the symmetrical constitution given above, and is consequently of little interest, has not been examined much further than was necessary for establishing its composition. Its *strychnine* salt is more soluble in water than the salt of the monosulphonic acid, and decomposes from about 226°. Its *l*-menthylamine salt is practically insoluble in light petroleum, and melts at 205–208°. The ammonium, sodium, and barium salts are crystalline.

The *strychnine* and the *l*-menthylamine salts of the *dl*-monosulphonic acid are not resolved during the prolonged course of fractional crystallisation which is necessary in separating them from the derivatives of the disulphonic acid. The *strychnine* salt crystallises well, and melts at 199°.

The *l*-menthylamine salt,



crystallises from moist light petroleum in lustrous plates, and is very similar in properties to the corresponding salts of the monosulphonic derivatives of benzylmethylethylpropylsilicane and benzylethylpropylisobutylsilicane. This fact was by no means promising, and seemed to indicate that attempts to resolve the new *dl*-acid would be just as unsuccessful as those already recorded in the case of the acids just mentioned. Fortunately, however, the great uncertainty of conclusions based on analogy in dealing with asymmetric compounds was again illustrated, as, after a few failures, the acid was easily resolved into its optically active components.

An account of the resolution experiments and of the properties of the active acids will be given in the near future.

EXPERIMENTAL.

Preparation of Dibenzylethylsilyl Chloride, $\text{SiEtCl}(\text{CH}_2\text{Ph})_2$.

Ethylsilicon trichloride (1 mol., 250 grams), diluted with about six times its volume of dry ether, and magnesium powder (1 atom) are placed together in a large flask, which is provided with a tap-funnel, a stirrer, and a suitable outlet tube.

A little benzyl chloride (2–3 c.c.) and a small quantity of an ethereal solution of magnesium benzyl chloride (prepared in a test-tube) are now added, and the flask is gently warmed. In a short time a reaction sets in, accompanied by the separation of magnesium chloride, and, as soon as this reaction becomes fairly vigorous, the flask is immersed in melting ice and the stirrer is started. Benzyl chloride (3 mols.) is then run in drop by drop, an operation which occupies about two and a-half hours; when the whole of it has been added, the contents of the flask are heated under a reflux condenser during three to four hours. After cooling the product, the granular precipitate of magnesium chloride is separated by filtration in absence of moisture (compare Kipping, Trans., 1907, 91, 216) and is washed several times with dry ether; on evaporating the combined ethereal filtrate and washings, there remains a yellow liquid, which fumes in moist air.

This liquid is first roughly fractionated under 100 mm. pressure from an ordinary distillation flask. Very little passes over below 165°, but between this temperature and 210° a fairly large fraction is collected. The thermometer then rises quickly to 238°, and another large fraction distils from 238° to 290°. Distillation may be continued up to 320°, or even higher, but this fraction has been only superficially examined; the dark green liquid which then remains in the flask is sometimes pasty, owing to the presence of magnesium chloride.

By systematically fractionating the liquid boiling between 165° and 210°, using a long-necked flask with a rod-and-disk column, benzylethylsilicon dichloride (Kipping, Trans., 1907, 91, 720) is obtained as an oil boiling at 168–170°/100 mm. The rest of the original distillate when similarly fractionated yields a liquid passing over between 246° and 251°/70 mm., almost the whole of which, however, boils constantly at 249°. The yield of this product is 40–50 per cent. of the theoretical. The fractions boiling at about 300°/40 mm. contain a small quantity of tribenzylsilyl chloride which separates in crystals on cooling. The formation of this substance is probably due to the presence of silicon tetrachloride in the ethylsilicon trichloride which was employed, and not to the displacement of an ethyl by a benzyl group; from a longer experience of silicon compounds it is concluded that such displacements, at one time thought to be possible (Robison and Kipping, Trans., 1908, 93, 440), do not occur.

The liquid boiling at $249^{\circ}/70$ mm. consists of dibenzylethylsiliclyl chloride. It was analysed by decomposing it with dilute ammonia and titrating the neutral solution with silver nitrate; 1 c.c. = 0.00309 gram Cl (Kipping, Trans., 1907, 91, 217):

0.9788 required 35.9 c.c. AgNO_3 . Cl = 12.8.

$\text{C}_{16}\text{H}_{18}\text{ClSi}$ requires Cl = 12.9 per cent.

Dibenzylethylsiliclyl chloride is an almost colourless oil, possessing, especially when freshly distilled, a fine bluish-violet fluorescence, which is probably due to traces of impurity. It has an aromatic, pungent odour, fumes in moist air, and is rapidly decomposed by water, giving dibenzylethylsilicol, which passes spontaneously into dibenzylethylsiliclyl oxide (m. p. 56°) when it is kept over sulphuric acid for a week or two.

Dibenzylethylpropylsilicane, $\text{SiEtPr}(\text{CH}_2\text{Ph})_2$.

Dibenzylethylsiliclyl chloride (1 mol., 170 grams) is mixed with an ethereal solution of magnesium propyl bromide ($1\frac{1}{10}$ mols.), and the ether is distilled off. Very little, if any, action takes place until most of the ether is removed, when a slight separation of magnesium chlorobromide is observed. The mixture is then heated for about two hours at 140 — 180° , at the end of which time it is cooled and treated with water. The oil which separates is extracted with ether and fractionated under 90 mm. pressure.

Distillation begins at about 250° , the thermometer quickly rising to 262° . Most of the product then passes over between 262° and 270° , and only a small quantity of high boiling residue remains in the flask. After further fractionation, pure dibenzylethylpropylsilicane, boiling at 262 — $265^{\circ}/90$ mm., is obtained. The yield is 70 to 80 per cent. of the theoretical:

0.1417 gave 0.4166 CO_2 and 0.1181 H_2O . C = 80.17; H = 9.24.

(A)* 0.2244 gave 0.0464 SiO_2 . Si = 9.7.

(B) 0.1202 „ 0.0253 SiO_2 . Si = 9.89.

$\text{C}_{10}\text{H}_{26}\text{Si}$ requires C = 80.68; H = 9.2; Si = 10.05 per cent.

The first samples of dibenzylethylpropylsilicane were prepared by the interaction of benzylethylpropylsiliclyl chloride and magnesium benzyl chloride. Benzylethylpropylsiliclyl chloride (1 mol., 20 grams) is added to an ethereal solution of magnesium benzyl chloride ($1\frac{1}{2}$ mols.), and, as no sign of a reaction occurs at this stage, the ether is distilled off and the residue is heated at about 140° during one to two hours. The pasty mass of oil and magnesium chloride is cooled and treated with water, and the oil extracted with ether.

When the crude product is distilled under 100 mm. pressure, it

* A and B were different preparations.

begins to boil at about 210° , and from this temperature to 240° a little dibenzyl passes over; the thermometer then rises rapidly to 260° , and the silico-hydrocarbon begins to distil. From the liquid collected between 260° and 280° , dibenzylethylpropylsilicane is obtained by further fractional distillation:

0.1948 gave 0.5790 CO_2 and 0.1628 H_2O . $\text{C} = 81.06$; $\text{H} = 9.3$.

0.4567 „ 0.0945 SiO_2 . $\text{Si} = 9.73$.

$\text{C}_{10}\text{H}_{22}\text{Si}$ requires $\text{C} = 80.68$; $\text{H} = 9.2$; $\text{Si} = 10.05$ per cent.

Although the yield by this method was very satisfactory, the task of preparing benzylethylpropylsilicetyl chloride, even in an approximately pure condition, is far more troublesome than that of preparing pure dibenzylethylsilicetyl chloride; for this reason, practically the whole of the silicane used in this investigation was obtained by the method described on p. 146.

Dibenzylethylpropylsilicane is a colourless liquid with a beautiful violet fluorescence. It has a pleasant aromatic odour, and is lighter than water. It is miscible with most organic solvents.

Sulphonation of Dibenzylethylpropylsilicane.

Knowing from previous experience (Kipping, Trans., 1907, 91, 223) that sulphuric acid is not a satisfactory sulphonating agent in the case of the silico-hydrocarbons, chlorosulphonic acid was used in the sulphonation of dibenzylethylpropylsilicane, and, as it seemed very likely that both benzyl groups might be attacked, chlorosulphonic acid ($1\frac{1}{2}$ mols.), dissolved in a large volume of chloroform, was gradually added to the well-cooled silicon compound, also in chloroform solution. When nearly two-thirds of this solution had been run in, a test portion of the product was poured into water and the chloroform was boiled off; repeating this test at intervals during the addition of the chlorosulphonic acid, the aqueous solutions of the product gradually altered in character. At first they contained visible drops of unchanged silico-hydrocarbon; later on, however, they were clear and apparently free from oil while hot, but became white and opaque when cooled, or they were white and opaque when hot but became quite clear on cooling.

Thinking that solubility in water was sufficient evidence that sulphonation was complete, and as it was very important not to use too large a quantity of chlorosulphonic acid, the addition of this reagent was generally stopped as soon as a sample of the product gave a clear solution in hot or cold water. Further investigation showed, however, that this test was not trustworthy, and that even when the sulphonation product gave a perfectly clear solution in water (after removing the chloroform by steam distillation), the

solution might nevertheless contain considerable quantities of unchanged silico-hydrocarbon; it was also found that when even the theoretical quantity (1 mol.) of chlorosulphonic acid was employed, a considerable quantity of disulphonic acid was formed.

In these circumstances various proportions of chlorosulphonic acid were tried, and the following method of preparation was finally adopted.

A solution of the hydrocarbon (b. p. 262—266°/90 mm.) in chloroform (6 vols.) is cooled in ice, and a solution of chlorosulphonic acid ($1\frac{1}{2}$ mols.) in chloroform (12 vols.) is added to it drop by drop while a rapid stream of dry carbon dioxide is passed through the mixture. Hydrogen chloride is evolved almost immediately, and the liquid soon assumes a red colour, which darkens slightly as the process continues.

After keeping the mixture at 0° for a short time, it is poured on ice, and, from the very slowly settling emulsion thus obtained, the chloroform is separated by steam distillation.

If the distillation is continued after all the chloroform has been removed, oil continues to pass over in small quantities during two or three hours. This oil is more quickly separated by extracting with ether; it consists almost entirely of unchanged dibenzylethylpropylsilicane, but sometimes contains relatively very small quantities of dibenzylethylsilicyl oxide (m. p. 56°), a fact which seems to show that the not very highly purified samples of the silico-hydrocarbon used in the preparation of the sulphonic acid contained small quantities of dibenzylethylsilicol.

The almost colourless aqueous solution of the sulphonic acid, which has been exhaustively extracted with ether, does not show the peculiar behaviour referred to above, which, therefore, must be attributed to the presence of the silicane. It is very remarkable, however, that the silicane should dissolve in an aqueous solution of the sulphonic acid.

Isolation of the Sulphonic Acids.

Many difficulties were met with in attempting to isolate the sulphonic acids produced in the manner described above. The ammonium salt was first prepared and freed from mineral salts by the method previously used in other cases (Kipping, Trans., 1907, 91, 225), but the crude salt was a syrupy or pasty substance, and could not be obtained in crystals. From the crude ammonium salt, many salts of organic bases were obtained by precipitation; of these, the strychnine salt alone gave crystalline deposits from suitable solvents, and consequently this base was first employed for the purpose in view.

In later experiments, when the properties of the sulphonic acids were known, *l*-menthylamine was used instead of strychnine, but as there is little to choose between the two methods, they are both described.

Method I.—The aqueous solution of the product of sulphonation is neutralised with sodium carbonate and treated with a concentrated solution of strychnine hydrochloride. The precipitate which is first produced dissolves on stirring, and, after some time, the solution acquires the appearance of raw white of egg, but on adding more strychnine hydrochloride a yellow oil is precipitated. The almost clear supernatant liquid is decanted, and the oil is then stirred with a little more of the solution of strychnine hydrochloride, after which it is extracted five or six times with boiling water and, lastly, with hot 8 per cent. aqueous acetone.

The remaining oil is then dissolved in alcohol, the solution diluted with about half its volume of water, and cooled in ice; the crystalline deposit which is thus obtained is further purified by repeated crystallisation from aqueous alcohol, and finally from anhydrous ethyl acetate containing a trace of acetone. This product is the strychnine salt of *d*-dibenzylethylpropylsilicanemonosulphonic acid.

The aqueous extracts of the crude strychnine salt, and also those obtained with 8 per cent. aqueous acetone, deposit white, asbestos-like needles, together with a considerable proportion of oil. After separating the crystals by the aid of the pump, the oil is again extracted twice with hot water, by which means a further quantity of the crystalline compound is obtained. The insoluble oily residue then consists principally of the strychnine salt of the monosulphonic acid, and is treated accordingly.

The salt which is soluble in hot water is dissolved in acetone, which contains a very small proportion of water, and the solution is allowed to evaporate spontaneously. The substance which is then deposited, after having been recrystallised from methyl alcohol, consists of the strychnine salt of dibenzylethylpropylsilicanedisulphonic acid.

Method II.—The aqueous solution containing the sodium salts of the sulphonic acids is treated with excess of a solution of *l*-menthylamine hydrochloride, and the precipitated oil is washed with water; this oil is then repeatedly extracted with boiling light petroleum (b. p. 40–60°). From these extracts the crude *l*-menthylamine salt of *d*-dibenzylethylpropylsilicanemonosulphonic acid is deposited in lustrous plates on cooling and stirring well with a little water.* This salt, however, still contains some *l*-menthylamine salt of the disulphonic acid, from which it is separated by repeated recrystallisation from moist light petroleum. In these operations, petroleum of very low boiling point gives the best results, because, although the pure *l*-menthylamine salt of the disulphonic acid is insoluble even in light

petroleum boiling at 60—80°, it dissolves to a considerable extent in presence of the salt of the monosulphonic acid.

That portion of the precipitated oil which is insoluble in light petroleum is dissolved in a small quantity of methyl alcohol, and treated with ethyl acetate until the well-stirred solution becomes very slightly turbid. If kept over sulphuric acid, nodular masses of the *l*-menthylamine salt of dibenzylethylpropylsilicanedisulphonic acid are deposited. From the mother liquors, a further amount of the *l*-menthylamine salt of the *dl*-monosulphonic acid can be obtained by evaporating them and extracting the residue with light petroleum.

Strychnine dl-Dibenzylethylpropylsilicanemonosulphonate.

This salt separates from aqueous alcohol or aqueous acetone in hydrated crystals, which melt below 100° and contain 3 molecules of water:

0.9125 of air-dried salt lost 0.0686 H_2O . $H_2O = 7.5$.

$C_{40}H_{48}O_5N_2SSi \cdot 3H_2O$ requires $H_2O = 7.2$ per cent.

When the hydrated salt is dissolved in ethyl acetate it quickly separates again in colourless needles, which still contain water of crystallisation and lose weight at 100°.

When heated, these do not soften until 160°, but resolidify above that temperature, and then melt at 199°, the melting point of the anhydrous salt.

The anhydrous salt was analysed:

0.1592 gave 0.4044 CO_2 and 0.0970 H_2O . $C = 69.2$; $H = 6.7$.

0.8305 „ 0.0717 SiO_2 . $Si = 4.06$.

$C_{40}H_{48}O_5N_2SSi$ requires $C = 68.9$; $H = 6.94$; $Si = 4.09$ per cent.

The anhydrous salt is only very slightly soluble in dry ethyl acetate, but dissolves readily in acetone, ethyl or methyl alcohol, chloroform, or toluene. It crystallises in leaflets from benzene, in which, however, it is very soluble. Short, stout, prismatic needles are obtained from a mixture of ethyl acetate and acetone. Light petroleum and ether have no solvent action.

The specific rotation of the anhydrous salt was determined in 98 per cent. methyl-alcoholic solution:

0.8771, made up to 25 c.c., gave, in a 2-dm. tube, $\alpha = 0.58^\circ$; whence $[\alpha]_D - 8.26^\circ$.

In spite of the fact that the isolation of this strychnine salt is only accomplished after a very laborious series of crystallisations from two solvents, the preparation melting at 199° is not a resolution product of the *dl*-monosulphonic acid, as will be shown later.

Conclusive evidence that the salt is really derived from dibenzyl-

ethylpropylsilicanemonosulphonic acid is afforded by the results of analyses of several other compounds prepared in the course of this investigation.

Strychnine Dibenzyloethylpropylsilicanedisulphonate.

The pure preparations of this compound, isolated in the manner already described, consist of a white, gritty powder, which turns brown at 226° and melts completely at 231°, above which temperature it rapidly decomposes.

Under the microscope it is seen to consist of short, rather ill-defined, prismatic needles:

0.1894 gave 0.4559 CO₂ and 0.1170 H₂O. C = 65.63; H = 6.86.

0.1780 „ 0.4293 CO₂ „ 0.1098 H₂O. C = 65.78; H = 6.86.

C₆₁H₇₀O₁₀N₄S₂Si requires C = 65.8; H = 6.35 per cent.

Owing to the slight solubility of the salt in 98 per cent. methyl alcohol, the specific rotation was determined in 90 per cent. methyl-alcoholic solution:

0.6162, made up to 25 c.c., gave, in a 2-dcm. tube, α = 0.75°; whence $[\alpha]_D$ = 15.21°.

Although the strychnine salt of the disulphonic acid might be expected to have a higher specific rotation than that ($[\alpha]_D$ = 8.26°) of the salt of the monosulphonic acid, it seemed probable that the very great observed difference might be due to the different proportions of water in the methyl alcohol employed in determining the two values.

This conclusion was confirmed by determining the specific rotation of strychnine dibenzyloethylpropylsilicanedisulphonate in methyl alcohol containing 36 per cent. of water:

0.5293, made up to 25 c.c., gave, in a 2-dcm. tube, α = 0.95°; whence $[\alpha]_D$ = 22.4°.

The salt is very sparingly soluble in cold methyl or ethyl alcohol, but is moderately soluble in the hot solvents, and also in boiling water; in ethyl acetate, acetone, benzene, and light petroleum it is practically insoluble, but it dissolves freely in chloroform and in aqueous acetone. The crystals deposited from aqueous solutions melt at about 110°, and are doubtless hydrated, as, when dried at 100°, their melting point rises to 226–231°.

1-Methylamine dl-Dibenzyloethylpropylsilicanemonosulphonate.

This salt crystallises from moist light petroleum in high lustrous plates containing 2 molecules of water of crystallisation. The hydrated salt liquefies at temperatures far below 100°, but when

kept over sulphuric acid it is completely dehydrated, and then melts at 99° :

1.3661 lost 0.0855 H_2O . $\text{H}_2\text{O} = 6.26$.

$\text{C}_{20}\text{H}_{47}\text{O}_5\text{NSSi}_2\cdot 2\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 6.55$ per cent.

The equivalent of the anhydrous salt was determined by boiling with excess of $N/50$ -sodium carbonate and then titrating with hydrochloric acid, using litmus as indicator. This method gave the value 516.4, that required by theory being 517.8.

The molecular weight of the anhydrous salt was determined by the cryoscopic method in benzene solution:

Substance.	Solvent.	E .	M.W.
0.795 gram	17.6 grams	0.12	1875

The calculated value is 517.8.

The molecular weight was also determined by the ebullioscopic method in methyl-alcoholic solution:

Substance.	Solvent.	E .	M.W.
0.089 gram	70.0 grams	0.035	305
0.207 "		0.075	332
0.348 "		0.130	322
0.723 "		0.260	334
1.006 "		0.360	336

These results correspond with those given in benzene and in methyl-alcoholic solutions respectively by the *l*-menthylamine salt of benzyl-methylethylpropylsilicanesulphonic acid (Kipping, Trans., 1907, 91, 737), and as the salt is doubtless highly ionised in the latter solvent, the observed values are such as might have been expected.

The specific rotation of the anhydrous salt was determined in methyl-alcoholic solution:

0.707, made up to 25 c.c., gave, in a 2-dm. tube, α -0.76° ; whence $[\alpha]_D - 13.4^{\circ}$.

l-Menthylamine *dl*-dibenzylethylpropylsilicanemonosulphonate is insoluble in water, but dissolves freely in all organic solvents. It may be recrystallised from aqueous alcohol and from aqueous acetone, but by far the most suitable solvent is petroleum of low boiling point; from this liquid the hydrated salt separates almost completely on cooling, but if the solution is boiled for some time, water is expelled, and the solution of the anhydrous salt does not deposit crystals until it has been stirred with water.

Metallic Salts of dl-Dibenzylethylpropylsilicanemonosulphonic Acid.

The sodium salt was prepared by decomposing the pure *l*-menthylamine salt with a slight excess of sodium carbonate and distilling off the liberated base in steam; the very great frothing which occurs in

the latter operation may be overcome by dropping alcohol continuously into the liquid.

On neutralising the residue with a few drops of acetic acid and evaporating, a soapy mass separates from the cold concentrated solution, but on adding water again and leaving the solution at the ordinary temperature, the salt is deposited in crystals; it is fairly readily soluble in cold water, and extremely so in alcohol. It is precipitated from its aqueous solution by sodium hydroxide, carbonate, or acetate.

The ammonium salt was obtained from the pure strychnine salt as a sticky mass on evaporating its aqueous solution. It is more readily soluble in water than the sodium salt, and its solution froths readily.

The barium salt was precipitated in flocculent, oily masses when a solution of the sodium salt was treated with a solution of barium chloride. It is only sparingly soluble in cold water or alcohol, but dissolves fairly readily in warm aqueous alcohol.

1-Methylamine Dibenzylethylpropylsilicane disulphonate.

This salt crystallises from a mixture of ethyl acetate and methyl alcohol in nodules, which contain water of crystallisation, but which, when anhydrous, melt at 205–208°.

The anhydrous salt is readily soluble in ethyl and methyl alcohols, but is insoluble in water, acetone, ethyl acetate, light petroleum, or benzene.

Metallic Salts of the Disulphonic Acid.

The ammonium salt of the disulphonic acid was prepared by treating a warm alcoholic solution of the strychnine salt with excess of ammonium hydroxide; on evaporation of the filtered solution it remained as a yellow solid, which was purified by recrystallisation from a mixture of ethyl acetate and methyl alcohol. It was thus obtained in lustrous plates, readily soluble in the common alcohols and in cold water, but insoluble in ethyl acetate, acetone, or light petroleum.

The equivalent of the compound was determined by boiling the salt with excess of $N/50$ -sodium carbonate, and then titrating the solution with acid. The results obtained were 239.4 and 237.4, the theoretical value being 238.4.

The sodium salt forms stellate crystals, and is readily soluble in water, fairly so in alcohol. In benzene, ethyl acetate, or acetone it is insoluble.

The barium salt was precipitated as a granular powder on adding a solution of barium chloride to a neutral solution of the ammonium

salt. It is sparingly soluble in water, and crystallises well from aqueous alcohol:

0.3594 gave 0.1445 BaSO_4 . $\text{Ba} = 23.67$.

$\text{C}_{19}\text{H}_{24}\text{O}_6\text{S}_2\text{SiBa}$ requires $\text{Ba} = 23.76$ per cent.

The authors are indebted to the Government Grant Committee of the Royal Society for a grant in aid of this research.

UNIVERSITY COLLEGE,
NOTTINGHAM.

XVII.—*The Influence of Various Substituents on the Optical Activity of Tartramide. Part III. Halogen-substituted Anilides.*

By PERCY FARADAY FRANKLAND and DOUGLAS FRANK TWISS.

In a previous communication (Trans., 1906, 89, 1852) we have given a list of the molecular rotations of the known tartramide derivatives, including the anilide and toluidides. In extension of this work we are now recording the results obtained with the chloroanilides and bromoanilides of tartaric acid, since it is of interest to study further the effect of substituents in the benzene ring of the anilide radicle. Previous investigations on asymmetric substances containing the benzene ring substituted in the different possible positions (for a list of papers see A. W. Stewart's *Stereochemistry*, p. 95; Betti, *Gazzetta*, 1907, 37, i, 62; and Pickard and Littlebury, Trans., 1907, 91, 300) have elicited the general result that the rotation of the isomerides stands in the order para \rightarrow meta \rightarrow ortho, exceptions being comparatively rare (compare Goldschmidt and Freund, *Zeitsch. physikal. Chem.*, 1894, 14, 394; also Frankland and Barrow, Trans., 1909, 95, 2031). The bromoanilides and chloroanilides described in this paper form no exception to the general rule, as is shown by the table given later.

In a previous communication on the ethyl and methyl esters of the *o*-, *m*-, and *p*-toluoyltartaric acids (Frankland and Wharton, Trans., 1896, 69, 1309 and 1583), it was also pointed out that the relative rotations of the ortho-substituted and of the unsubstituted aromatic compounds respectively appear to depend on both the centre of gravity of the chain attached to the asymmetric atom, and also on the increase in mass of the chain. If the loss in leverage is not compensated sufficiently by the increase in mass, the rotation of the substituted

molecule will be less than that of the unsubstituted; this was the case with the substitution of methyl in the ortho-position in benzoyl-tartaric esters.

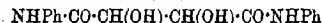
In the case of the anilides of tartaric acid, the substitution of methyl, bromine, or chlorine in the ortho-position lowers the molecular rotation; in the meta-position, the substitution of methyl causes a slight diminution, but the heavier chlorine or bromine an increase in the molecular rotation. This result is in all probability due mainly to the effect of the superior mass of the bromine and chlorine atoms, but may also be assisted to some extent by the negative character of these atoms, as explained later.

The following table gives the values for the molecular rotations (in pyridine solution) of the chloroanilides and bromoanilides, together with those already published for the toluidides and the anilide, the latter being included for the sake of comparison.

$[M]_D^{20}$ dianilide.	$[M]_D^{20}$ ditoluidide.	$[M]_D^{20}$ dibromoanilide.	$[M]_D^{20}$ dichloroanilide.
+738°	ortho +687° meta +730 para +793	+652° +867 +886	+709° +824 +838

A remarkable fact shown by these numbers is that, whilst the replacement of the ortho-hydrogen atom by methyl causes a lowering in the molecular rotation, replacement by the heavier substituent chlorine causes a much smaller decrease, and even the bromine atom hardly lowers the rotation of tartranilide more than the methyl group.

Again, it is noteworthy that in the series toluidide \rightarrow bromoanilide \rightarrow chloroanilide, the difference between the values of the meta- and para-isomerides becomes less. This effect, together with the one previously mentioned, is possibly due to the increase in the negative character of the substituent; we would suggest that the negative substituent in the meta-position of the benzene ring is attracted (probably by one of the hydrogen atoms in the tartaric acid nucleus) in such a direction that the resulting distortion increases the asymmetry, whilst with the negative atom in the para-position the differently directed attraction causes such distortion that the asymmetry is decreased. Thus the more negative the substituent, the more closely will the rotations of the meta- and para-isomerides approximate to one another. That this explanation is at least a reasonable one is seen by constructing a graphic formula of the most compact configuration of the molecule, with the bonds drawn to the correct angles and to lengths in accord with Traube's atomic volumes. In such a formula the chain $C \cdot CH \cdot CO \cdot NHPh$ of the molecule



will be found to form an almost closed ring, the hydrogen attached

to the one asymmetric carbon atom falling near the benzene ring and actually between the meta- and para-positions of the chain attached to the other asymmetric atom. Any attraction between this hydrogen atom and a halogen atom in the para-position of the benzene ring will cause an increased compactness of the molecule, and so lessen the asymmetry. On the other hand, an attraction between this hydrogen and a negative atom in the meta-position will lead to a distortion outwards, from the tartaric nucleus, and so cause an outward displacement of the $\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{X}$ chain, with a corresponding increase in asymmetry.

A halogen atom in the ortho-position would probably be so far removed from the hydrogen of the other asymmetric atom that the attraction would be much less; nevertheless, the experimental results seem to indicate that even this has an appreciable effect in increasing the asymmetry.

In connexion with this hypothesis it is of interest to compare the rotation of the *m*-iodotartranilide* with that of the other meta-substituted tartranilides.

	Dianilide.	Di- toluide.	Dichloro- anilide.	Dibromo- anilide.	Di-iodo- anilide.
$[\text{M}]_D^{20}$ (in pyridine solution)	739°	780°	824°	867°	888°
Increase in rotation	-9°		94°		43°
Increase in mass (for one chain)	14		20.5		47

The increase in $[\text{M}]_D$ is greatest for one of the smallest changes in mass, and it is remarkable that it is between the neutral methyl and the negative chlorine. For the increase in optical activity between the chloro- and bromo-anilide, the mass-increase is the cause, the inferior negativity of the bromine atom reducing the $[\text{M}]_D$ and so giving rise to a smaller increment in activity. Again, the diminished negativity of the iodine atom would be the reason for the greatest increase in mass (47) being attended, nevertheless, by the smallest increment in activity.

In the preparation of the compounds described in this paper, great care was taken to ensure a pure product. Each substance, where possible, was prepared in two ways (from the free acid and from the methyl ester), and the product was in each case recrystallised until of constant specific rotation. The majority of the rotations were measured in approximately 5 per cent. solution in dry pyridine at 20°. Concentration was found to have little influence on the optical activity. The substances were all crystalline solids of high melting point (185–276°).

* Prepared by Mr. Norton in this laboratory; this, with other iodoanilides, will form the subject of a future communication.

EXPERIMENTAL.

Tartarodi-p-bromoanilide.

This was prepared by heating together powdered tartaric acid and *p*-bromoaniline (Kahlbaum) in theoretical proportions at 150—160° for fifteen hours. After extracting with boiling dilute hydrochloric acid and with water, the residue was repeatedly crystallised from a mixture of alcohol and pyridine (7:3 by volume).

The following figures show the rotation observed in pyridine solution :

<i>p</i> .	<i>d</i> 20°/4°.	<i>l</i> (dms.).	$\alpha_D^{20^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
4.902	1.0004	1.998	+18.95°	+193.4°	+886°

The substance was also prepared by heating together theoretical proportions of methyl tartrate and *p*-bromoaniline to 130—140° for ten hours. After similar purification to that described above, the product gave the following rotation in pyridine solution :

4.908	1.0008	1.998	+18.95°	+193.2°	+885°
-------	--------	-------	---------	---------	-------

The rotation in methyl alcohol is not suited for exact measurement on account of the low solubility of the substance; the result, however, indicates a distinctly lower rotatory power than that in pyridine solution :

0.1359	0.792	3.899	+0.76°	+181.1°	+829°
--------	-------	-------	--------	---------	-------

The specimens of bromoanilide prepared by the above methods had the same melting point, namely, 264° with decomposition; the substance forms slender crystals (elongated flat plates), which become matted together so as to give rise to a tough white solid resembling paper. It is insoluble in water, sparingly soluble in most of the ordinary solvents, but readily so in pyridine :

0.2429 gave 12.68 c.c. N_2 (moist) at 11.8° and 754 mm. $N = 6.12$.

$C_{10}H_7Br_2O_4N_2$ requires $N = 6.12$ per cent.

Tartarodi-m-bromoanilide.

As with the para-compound, this was prepared by the two independent methods. The tartaric acid and *m*-bromoaniline (Kahlbaum) were heated to 150—160° for ten hours, and the methyl tartrate and base to 130—140° for the same period. The product is more soluble in alcohol than the para-compound, and, after extraction with dilute hydrochloric acid, was purified by recrystallisation from this solvent.

The following numbers give the rotation observed in pyridine solution:

(a) Preparation from tartaric acid and *m*-bromoaniline:

<i>p.</i>	<i>d</i> 20°/4°.	<i>l</i> (dms.).	α_D^{20} .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
4.817	0.9995	1.998	+18.22°	+189.4°	+867°

(b) Preparation from methyl tartrate and *m*-bromoaniline:

4.835	0.9994	1.998	+18.28°	+189.3°	+867°
-------	--------	-------	---------	---------	-------

The rotation of the specimen prepared from tartaric acid was also measured in methyl-alcoholic solution:

0.9862	0.7981	3.899	+4.74°	+154.5°	+707°
--------	--------	-------	--------	---------	-------

The *m*-bromoanilide crystallises in small, hard, flat plates, which melt at 220° with slight decomposition:

0.2716 gave 14.3 c.c. N_2 (moist) at 13° and 753 mm. $N = 6.14$.

$C_{10}H_{14}O_4N_2Br_2$ requires $N = 6.12$ per cent.

Tartarodi-o-bromoanilide.

This substance was prepared only from tartaric acid and *o*-bromoaniline, the mixture of methyl tartrate and *o*-bromoaniline undergoing extensive decomposition on heating. Approximately theoretical proportions of tartaric acid and *o*-bromoaniline (from reduction of *o*-bromonitrobenzene: Fittig and Mager, *Ber.*, 1874, 7, 1179) were heated to 150—160° for twenty hours. The resultant mass was purified by treatment similar to that in the previous cases, and, finally, repeatedly recrystallised from a mixture of alcohol and water (3:2 by volume) with simultaneous decolorisation by animal charcoal.

The optical activity was measured in pyridine and in methyl alcohol:

(a) In pyridine:

<i>p.</i>	<i>d</i> 20°/4°.	<i>l</i> (dms.).	α_D^{20} .	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
6.604	1.0076	0.999	+9.46°	+142.3°	+652°
4.572	0.9989	0.999	6.53	143.1	656

(b) In methyl alcohol:

3.363	0.8076	0.999	+3.21°	+113.3°	+542°
0.9402	0.7964	2.993	2.71	120.9	554

The *o*-bromoanilide consists of colourless, thin, rectangular needles, which melt at 193° without decomposition; it is very soluble in pyridine and in hot alcohol, and sparingly so in hot water:

0.2410 gave 12.9 c.c. N_2 (moist) at 17.5° and 745 mm. $N = 6.04$.

$C_{16}H_{14}O_4N_2Br_2$ requires $N = 6.12$ per cent.

Tartarodi-p-chloroanilide.

The method of preparation was similar to that of the corresponding bromoanilide; the substance was purified by recrystallisation from a mixture of 1 volume of pyridine to 3 of alcohol.

Preparation from tartaric acid, in pyridine solution :

<i>p.</i>	<i>d</i> 20°/4°.	<i>l</i> (dms.).	$\alpha_D^{20^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
4.605	0.9939	1.998	+20.77°	+227.1°	+338°

Preparation from methyl tartrate, in pyridine solution :

5.015	0.9957	0.999	+11.34°	+227.3°	+339°
-------	--------	-------	---------	---------	-------

The rotation in methyl-alcoholic solution was much lower than that observed in pyridine, although the low solubility increases the probability of error in the specific rotation :

0.1749	0.7943	3.699	+1.06°	+196°	+722°
--------	--------	-------	--------	-------	-------

The *p*-chloroanilide forms needle-shaped crystals, melting and decomposing at 276° :

0.2035 gave 13.6 c.c. N_2 (moist) at 12.6° and 748 mm. $N = 7.75$.

$C_{16}H_{14}O_4N_2Cl_2$ requires $N = 7.59$ per cent.

Tartarodi-m-chloroanilide.

The reaction, both in the case of the preparation from the acid and *m*-chloroaniline (Kahlbaum), as well as in that from the ester and base, appeared to proceed less rapidly than in the production of *m*-bromoanilide, and involved heating for sixteen hours. After the usual preliminary treatment, the product was recrystallised from a mixture of 1 volume of water with 3 of alcohol.

The specimen from tartaric acid and *m*-chloroaniline gave the following rotation in pyridine solution :

<i>p.</i>	<i>d</i> 20°/4°.	<i>l</i> (dms.).	$\alpha_D^{20^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
4.966	0.9953	0.999	+11.03°	+223.4°	+324°
1.746	0.9829	2.993	11.42	222.3	820

whilst that from methyl tartrate and the base gave the following figures :

4.865	0.9949	0.999	+10.60°	+223.4°	+324°
-------	--------	-------	---------	---------	-------

The rotation in solution in methyl alcohol was as follows :

1.504	0.7871	2.993	+6.54°	+182.3°	+673°
-------	--------	-------	--------	---------	-------

Tartarodi-m-chloroanilide crystallises in thin, fibrous needles, which melt and decompose slightly at 212° :

0.2035 gave 13.7 c.c. N_2 (moist) at 13° and 736 mm. $N = 7.66$.
 $C_{16}H_{14}O_4N_2Cl_2$ requires $N = 7.59$ per cent.

Tartarodi-o-chloroanilide.

As in the case of the corresponding *o*-bromoanilide, the preparation of this substance was attended with more difficulty than that of the meta-compound; the mixtures had to be heated for twenty hours, and the yields were inferior to those obtained in the case of any of the other anilides. The yield from the ester was particularly poor, the crude product being a black, pasty mass. For the recrystallisation a mixture of one part of water to two of alcohol was employed.

The following are the rotations obtained in pyridine solution:

(a) Specimen prepared from tartaric acid:

p .	$d\ 20^\circ/4''$.	l (dms.).		$[\alpha]_D^{20}$.	$[\alpha]_D^{25}$.
4.881	0.9944	0.999	+9.32°	+192.2°	+709°
1.392	0.9816	2.993	7.89	192.9	712

(b) Specimen from methyl tartrate:

5.060	0.9940	0.999	+9.65°	+192.1°	+709°
-------	--------	-------	--------	---------	-------

The optical activity was measured also in methyl alcohol:

1.524	0.7980	2.993	+5.98°	+164.3°	+608°
-------	--------	-------	--------	---------	-------

The *o*-chloroanilide crystallised in long, narrow plates, melting at 185° . It is sparingly soluble in hot water, but very soluble in pyridine and in hot alcohol:

0.2067 gave 13.75 c.c. N_2 (moist) at 14° and 748 mm. $N = 7.67$.

$C_{16}H_{14}O_4N_2Cl_2$ requires $N = 7.59$ per cent.

UNIVERSITY,
BIRMINGHAM.



THOMSEN MEMORIAL LECTURE.

DELIVERED ON FEBRUARY 17TH, 1910.

EDWARD THORPE, C.B., LL.D., F.R.S., Past-President of the
Chemical Society.

the Danes whose names are inscribed as men of science on the national bead-roll of fame, that of Julius Thomsen stands pre-linked indeed with that of Oersted. It is significant of the position which Thomsen acquired in physical science, and of the respect which that position secured for him in the eyes of his fellow-citizens, that his statue should have been erected during his lifetime and placed in the vicinity of that of Oersted in the courtyard of the Polytechnic High School of Copenhagen. Thomsen, in many respects, played many parts in the intellectual, industrial, and social life of Denmark. To Europe in general he was mainly known as a distinguished man of science. By his fellow-citizens he was further recognised as an educationist of high ideals, actuated by common sense and a stern devotion to duty; as an able and sagacious administrator; as a successful technologist and the founder of an important and lucrative industry based upon his discoveries; and as a man of forceful character, who brought authority, skill, and knowledge of men and affairs to the service of the communal life of Copenhagen.

Thomsen was a municipal councillor of that city for more than half a century. He occupied a commanding position on the town council and was invariably listened to with respect. The gas, water, and sewage works of Copenhagen are among the monuments of his civic activity. From 1882 up to the time of his death he was a member of the Harbour Board of the port. In these respects he sought to realise Priestley's ideal of the perfect man—that he should be a good citizen first and a man of science afterwards.

Peter Jürgen Julius Thomsen was born in Copenhagen on July 16th, 1826. He was educated at the church school of his native town in that city, and subsequently at von Westens Institute. There he commenced his studies at the Polytechnic, and in 1846 moved there in Applied Science, and became an assistant to Professor E. A. Scharling. Of his earliest years comparatively little is known. Thomsen, always a reserved and taciturn man, wrote little about himself even to his intimate friends—and least about the days of his youth. It was known to a few that his days had not been smooth. Those who were best informed

were conscious that to these early struggles much of that dour and resolute nature which formed a distinguishing trait in his character was due. Thomsen, indeed, began life as a fighter, and a fighter he remained to the end of his four-score years.

In 1847, he became assistant to Forchhammer, passing rich, like Goldsmith's pedagogue, on £40 a year. Georg Forchhammer, whose earliest work dates back to the period when Berzelius was in his prime, was an active and industrious investigator of the old school, mainly in inorganic chemistry, and more particularly on problems of chemical geology and physiography. He was a frequent visitor to this country, and was well known to early members of the British Association. Although doubtless influenced, in common with all teachers in Northern Europe, by the example and methods of Berzelius, such influence as he himself was able to exert died with him. Forchhammer attracted few pupils, and created no school, and Thomsen probably derived no inspiration or acquired any stimulus from this association. For a time Thomsen supplemented his scanty income by teaching agricultural chemistry at the Polytechnic. In 1853 he obtained a travelling scholarship, and spent a year in visiting German and French laboratories. He probably owed this scholarship in great measure to his first contribution to the literature of chemistry, namely, his memoir, "Bidrag til en Thermochemisk System" (contributions to a thermochemical system), communicated to the Royal Society of Sciences of Copenhagen in 1852, and for which he received the silver medal of the Society and a sum of ten guineas to enable him to procure a more accurate apparatus. In this memoir he sought to develop the chemical side of the mechanical theory of heat, doubtless under the influence of Ludwig Augustus Colding, an engineer in the service of the Municipality of Copenhagen, and a pioneer, like Mayer, in the development of that theory. Indeed, the Danes now claim for Colding, who had made experiments on the relation between work and heat as far back as 1842, but whose labours were practically ignored by his contemporaries, the position which the Germans assign to Mayer (see Mach's "Development of the Theory of Heat"). In 1861 Thomsen further developed his ideas in a memoir on the "General Nature of Chemical Processes, and on a Theory of Affinity Based Thereon," published in the Transactions of the Danish Academy of Sciences. In this paper he laid the foundations of the chief scientific work of his life.

In 1853 Thomsen patented a method of obtaining soda from cryolite, so-called "Greenland," or ice-spar, a naturally occurring fluoride of sodium and aluminium, $\text{Al}_2\text{F}_6 \cdot 6\text{NaF}$, found largely, indeed, almost exclusively, in Greenland, and particularly at

It derives its mineralogical name from its ice-like appearance and ready fusibility even in the flame of a candle. It was to have been first brought to Europe in 1794, and to have been described by Schumacher in the following year. Klaproth first showed that it contained soda, and its composition was further established by Vauquelin, Berzelius, and Deville. Thomsen's process consists in heating a finely divided mixture of potash and chalk in a reverberatory furnace, whereby carbon dioxide is expelled and calcium fluoride and sodium aluminate are formed. The roasted mass is lixiviated with water, so as to dissolve out the sodium aluminate, which is then treated with carbon dioxide. Alumina is precipitated, and sodium carbonate remains in solution. The alumina is either sold as such, or converted into sulphate (so-called "concentrated alum" or "alum-ke"), and the sodium carbonate is separated by crystallisation. Both products are obtained in a remarkably pure condition, and the potash-soda yields excellent "caustic."

Thomsen's process, although simple enough in principle, requires considerable skill and pains in its practical execution, and most of the manufacturing details were worked out by him, or under his direction. Success largely depends upon the maintenance of a proper temperature; the decomposition begins below a red-heat, but requires to be finished at that temperature, and care must be taken to avoid fusion or even sintering of the mass. In 1854 Thomsen obtained the exclusive right of mining for cryolite and of working the mineral in Denmark for soda and alumina. Actual manufacturing operations were begun on a small scale in 1857, and in the following year Thomsen planned the present large factory at Esbjerg, near Copenhagen, which was opened on his thirty-fourth birthday. The importance of this industry to Denmark may be seen from the circumstance that during the fifty years of its existence the firm have paid the Danish Government nearly 100,000 for the concession. Other factories were started in Germany, Bohemia, and Poland, but met with little success. The Pennsylvania Salt-manufacturing Company at Natrona, near Gettysburg, eventually obtained the right to work up two-thirds of the cryolite mined in Greenland. From the start Thomsen took a large share in the management of the Oeresund works, and by his energy, foresight, and skill placed the undertaking on a sound commercial basis.

Although Thomsen died a rich man, mainly as the result of the industry he created, in the outset of his career as a teacher and a chemist his means were very straitened. He came of poor parents, of no social position or influence, and they were unable to

further his inclinations towards an academical career. In 1854 he applied unsuccessfully for a position as teacher of chemistry at the Military High School in Copenhagen. During three years—from 1856 to 1859—while still engaged in developing his cryolite process, he acted as an adjuster of weights and measures to the Municipality of Copenhagen. It was a poorly paid position, but it kept the wolf from the door. At about this period he betook himself to literature, and published a popular book on general subjects connected with physics and chemistry—somewhat in the style of Helmholtz's well-known work—entitled "Travels in Scientific Regions," which had a considerable measure of success. He was, however, not altogether unknown even at this time as an author, since in 1853 he had collaborated with his friend Colding in producing a memoir on the causes of the spread of cholera and on the methods of prevention, which attracted much attention at the time of its appearance.

In 1859, whilst engaged in the Oeresund factory, he again applied to the authorities for a position as teacher at the Military High School, and succeeded in obtaining an appointment to a lectureship in physics, which he held until 1866. During his tenure of this office he devised his polarisation battery, which received many awards at International Exhibitions and was used for a time in the Danish telegraph service.

In 1859-60 he was "vicarius" for Scharling at the University and in 1865 became a teacher, and in the following year Professor of Chemistry and Director of the Chemical Laboratory, a position which he retained—active to the last—until 1901, when he retired in his seventy-fifth year of age.

Before his connexion with the University, he founded and edited from 1862 to 1878, in association with his brother, August Thomsen, the *Journal of Chemistry and Physics*, one of the principal organs of scientific literature in Denmark.

In 1863 he was elected a member of the Commission of Weights and Measures, and was instrumental in bringing about the adoption of the metric system and the assimilation of the Danish system to that of the Scandinavian Kingdom.

In 1883 Thomsen became Chancellor of the Polytechnic High School of Copenhagen—a position which he held for about nine years. During this period he entirely changed the character and spirit of the school, and stamped it with the impress of his earnestness and industry. Under his direction, new buildings were erected and arranged in accordance with the best Continental and American models. Thomsen's administration was in marked contrast to that of his somewhat easy-going predecessor, but it is doubtful if

brought him popularity in the school. The students respected and even feared him, but his cold and unsympathetic nature evoked a warmer feeling. It was said of him by one who knew him intimately that he never learned to draw the young to him, to reate in them an interest for his work, to form a school. Thomsen was a homely man, but not even in his home, says the same authority, was it possible for him to change his active, earnest, trepicious disposition—what his friends called his fighting character. but if he was always the serious master of the house, he was also a obedient servant. In reality he was a man of deep feeling, and as not without power to give that feeling expression in words, sometimes in verse, and occasionally even in music.

It was while occupying the position of Director of the Chemical laboratory of the University that Thomsen executed the thermochemical investigations which constitute the experimental development of the ideas he had formulated in his memoir of 1861. The results of these inquiries were first made known in a series of apers published from 1869 to 1873 in the Transactions of the Royal anish Society of Sciences, and from 1873 onwards by the *Journal ir Praktische Chemie*. The papers were republished in collected orm in four volumes (1882-1886) by a Leipzig house under the ile of *Thermochemische Untersuchungen*. A summary of this xperimental labour, which extended over a third of a century, as subsequently prepared by Thomsen, and published in 1905 in anish under the title of *Thermokemiske Resultater*.

In this work he reviewed the whole of the numerical and aeoretical results, to the exclusion of the greater portion of the xperimental details. A translation of this volume by Miss atharine A. Burke, entitled "Thermochemistry," renders it adily accessible to English readers. Miss Burke has supple- ented the original work by a short account, taken from the *hermochemische Untersuchungen*, of the experimental methods ployed, thereby rendering the whole more intelligible to the udent. Moreover, in the English edition a partial attempt has een made to translate Thomsen's deductions into the language of odern theory based on the conception of ionisation, which, of urse, was not known to science at the time the *Thermochemische ntersuchungen* was published.

It is impossible within the limits of such a notice as this to deal t detail with the immense mass of experimental material which is work embodies, and I shall not attempt, therefore, to do more an to offer a generalised statement, based mainly upon the mirable account of Thomsen's work given by Professor Brönsted t the Chemical Society of Copenhagen on the occasion of the

meeting held on March 2nd, 1909, to commemorate Thomsen's services to science.

The conception of affinity as a cause and determining condition of chemical change is traceable in some of the earliest efforts to co-ordinate and explain chemical phenomena. It certainly existed long prior to the time of Boyle, and was at the basis of every philosophical system after his period. We need only mention the names of Bergman, Wenzel, and Berthollet to indicate this fact. But to Thomsen belongs the credit of being the first to make the attempt to measure the relative value or strength of affinity quantitatively, and to express it numerically in definite terms which admitted of exact comparison. Thomsen's theory of affinity, as enunciated by him in his 1851 paper, was based upon his conviction that affinity could be measured quantitatively by estimating the amount of heat evolved in the chemical process. We are not immediately concerned to show whether the theory is right or wrong, or in what respect it fails. The point is that the enunciation of this principle upwards of half a century ago constituted an important step forward, inasmuch as it sought to estimate affinity in relation to a quantity which can be fixed by experiment, and is capable of expression by numbers.

In this and in the subsequent paper of which mention has been made already, he thus defines his conception of thermochemistry, and discusses, for the first time, its laws.

"The force which unites the component parts of a chemical compound is called affinity. If a compound is split up, whether by the influence of electricity, heat, or light, or by the addition of another substance, this affinity must be overcome. A certain force is required the amount of which depends on the strength of the affinity.

"If we imagine, on the one side, a compound split up into its component parts, and on the other side these parts again united to form the original compound, then we have two opposite processes the beginning and end of which are alike. It is therefore evident that the amount of the force required to split up a certain compound must be the same as that which is evolved if the compound in question is again formed from its component parts.

"The amount of force evolved by the formation of a compound can be measured in absolute terms; it is equal to the amount of heat evolved by the formation of the compound.

"Every simple or complex action of a purely chemical nature is accompanied by evolution of heat.

"By considering the amount of heat evolved by the formation of a chemical compound as a measure of the affinity, as a measure

of the work required again to resolve the compound into its component parts, it must be possible to deduce general laws for the chemical processes, and to exchange the old theory of affinity, resting on an uncertain foundation, for a new one, resting on the sure foundation of numerical values."

As has been proved by later theoretical and experimental investigations, the theory of thermochemical affinity is not absolutely correct at ordinary temperatures. But, on the other hand, it has been shown that a comparatively large number of processes are approximately in unison with it. Not only do they agree qualitatively, that is to say, that heat is evolved during the process, but also in the fact that the results which newer and more exact methods for estimating affinity have produced, agree numerically with what would be required by the thermochemical theory. We meet here with a fundamental phenomenon which Thomsen deserves great credit for having first pointed out, but the explanation of which could not be given at the time he indicated it. It can be demonstrated theoretically that the lower we reduce the temperature and the nearer we get to the absolute zero, the more nearly is the condition for the theory fulfilled, so that at the absolute zero the theory would be found to be an exact law of nature. If it were possible to work at such low temperatures it would be found that the evolution of heat, or the evolution of energy by the chemical process, would be an exact measure of the affinity of the process, and that under this condition the theory of Thomsen would be the accurate expression of a natural law.

But under ordinary conditions this is not so, for in reality an ever-increasing number of endothermic processes are found to occur, that is, processes which proceed with the absorption of heat. Thomsen tried at first to explain these phenomena in such a way as to keep them within his system, and he drew a distinction between a purely chemical process running conformably to, his theory and a physico-chemical process which did not fall within the law. But he was gradually convinced that his theory could not be maintained in its entirety. It is to his credit that he did not seek to uphold an untenable principle, or try to defend it as did Berthelot, who almost to his dying day maintained the validity of the principle in spite of all facts.

These ideas have, in the words of Ostwald, been the scientific confession of faith of chemists throughout half a century. They have had the greatest influence on scientific thought in every branch of chemistry. It is on the basis of them that we have arrived at a theory of affinity which at the present moment is being developed into one of the most perfect chemical theories.

Lastly, it is due to these ideas that the experimental material has been produced which during all time will place the name of Julius Thomsen in the first rank of men of science.

To go through this material in detail is, as I have said, impossible here. It may be stated generally that practically every simple inorganic process has been investigated calorimetrically, by Thomsen, or can be calculated by means of the calorimetric data furnished by him. In the case of organic substances, data have been given for estimating the heat of combustion of a large number of compounds. All these estimations were made by Thomsen personally, according to a pre-arranged plan, and in systematic succession during a period of more than thirty years. They comprise more than 3500 calorimetric estimations. It has been truly said that this work is unique in the chemical history of any country.

Among the results of Thomsen's thermochemical inquiries which have special value for physical chemistry is his investigation of the phenomena of neutralisation, in which he shows that the basicity of acids can be estimated thermochemically, and that it can in this way be proved whether or not a point of neutrality exists. His observation that the heat of neutralisation is the same for a long series of inorganic acids, such as hydrochloric acid, hydrobromic acid, hydriodic acid, chloric acid, nitric acid, etc., supports the theory of electrical dissociation, inasmuch as this requires that the heat of neutralisation of the strong acids must in all cases be independent of the nature of the acid, because the process of neutralisation for all of them is the combination of the ion of hydrogen in the acid with the ion of hydroxyl of the base to form water. These investigations also led to the important thermochemical result that the heat of neutralisation of acids (or the heat of their dissociation) cannot be considered as a measure of the strength of the acids.

Another important result is the proof by experiment of the connexion which exists between the changes of the heat-effect with the temperature and the specific heat of the reacting substances. The first law of thermodynamics requires the relation indicated

by Kirchhoff: $\frac{dU}{dT} = C_1 - C_2$, where U is the heat-effect, T the

temperature, and C_1 and C_2 are the heat capacities of the two systems before and after the reaction, and Thomsen showed by investigation of the heat of neutralisation, the heat of solution, and the heat of dilution, that this relation was satisfied. For the purpose of his inquiry, the specific heats of a large number of solutions of salts were estimated by an ingenious method, and with an exactness hitherto unattained.

Of no less importance are Thomsen's thermochemical investigations on the influence of mass. In the year 1867 Guldberg and Waage published their theory of the chemical effect of mass. But they had only verified the theory to a small extent and in particularly simple cases. They had not investigated the complete homogeneous equilibrium, because at that time no method existed for experimental investigation of such homogeneous equilibrium. Thomsen showed that the estimation could be made thermochemically. By allowing, for instance, an acid to act on a salt of another acid in an aqueous solution, the latter acid will be partly replaced by the first, which will form a salt. By mixing, for instance, a solution of sodium sulphate and nitric acid, there is formed sodium nitrate and sulphuric acid, but the process will not proceed to completion. If we have estimated the heat of neutralisation of the two acids with sodium hydroxide, the difference between these two heat-phenomena will give the amount of heat corresponding to the total decomposition of the sodium sulphate, and the heat found experimentally by mixing the two solutions will therefore show to what degree the transformation has taken place. It would be possible to estimate thermochemically the amount of the four substances in solution, and thereby, by varying the concentration or the proportion between the initial quantities of substances, to calculate whether the Guldberg-Waage theory on the effect of mass was confirmed in this case.

Thomsen applied this method to a large number of different acids and bases, and was enabled thereby to prove the agreement with the law of the influence of mass in all the cases which he examined. He found particularly that the proportion of the one acid which remained combined with the base was constant with mixtures of constant proportion. On this basis he propounded the term *avidity*, which he defined as the tendency of the acid to unite with the base, and he showed that the avidity was independent of the concentration, and only to a small extent varied with the temperature. The term *avidity* has since acquired great importance, particularly since other and more exact methods for its estimation have been found. Concurrently with this, its meaning has been made clear by the theory of electrolytic dissociation.

On the basis of these estimations, Thomsen drew up the first table, based on experiments, of the relative strength of the acids, and the numbers in this table have been found to agree with the results obtained by examining the electrical conductivity of the acids.

It is worth noting that Thomsen not only produced the experimental proof of the correctness of the Guldberg-Waage theory of

the effect of mass soon after the appearance of this theory, but also that he was the first to acknowledge and adopt it. It is remarkable that this work of Thomsen received so little attention, although it appeared in a widely circulated German journal, and it was not until ten years later that the law of the effect of mass was generally recognised, as the result of the work of Ostwald and van't Hoff.

Although Thomsen's title to scientific fame rests mainly upon his thermochemical work, his interests extended beyond this particular department of physical chemistry. He worked on chloral hydrate, selenic acid, on ammoniacal platinum compounds, and on glucinum platinum chloride, on iodic acid and periodic acid, on hydrogen peroxide, hypophosphorous acid, and hydrogenium. He early recognised the importance of Mendeléeff's great generalisation, and contributed to the abundant literature it produced. His paper of 1895, "On the Probability of the Existence of a Group of Inactive Elements," may be said to have foreshadowed the discovery of the congeners of argon. He pointed out that in periodic functions the change from negative to positive value, or the reverse, can only take place by a passage through zero or through infinity; in the first case, the change is gradual, and in the second case it is sudden. The first case corresponds with the gradual change in electrical character with rising atomic weight in the separate series of the periodic system, and the second case corresponds with a passage from one series to the next. It therefore appears that the passage from one series to the next in the periodic system should take place through an element which is electrically indifferent. The valency of such an element would be zero, and therefore in this respect also it would represent a transitional stage in the passage from the univalent electronegative elements of the seventh to the univalent electropositive elements of the first group. This indicates the possible existence of a group of inactive elements with the atomic weights 4, 20, 36, 84, 132, the first five numbers corresponding fairly closely with the atomic weights respectively of helium, neon, argon, krypton, and xenon (*Zeitsch. anorg. Chem.*, 1895, 9, 283; *Journ. Chem. Soc.*, 1896, 70, II, 16). He subsequently made known the existence of helium in the red fluoride from Ivigtut.

As evidence of Thomsen's manipulative ability and his power of accurate work may be mentioned his determination of the atomic weights of oxygen and hydrogen, and incidentally of aluminium. For the atomic weight of hydrogen he obtained the value 1.00825 when $O=16$, which is practically identical with that of Morley and Noyes. He further made most accurate estimations of the relative

densities of these gases, and of the volumetric ratios in which they enter into the composition of water. His value for the atomic weight of aluminium is nearly identical with that adopted in the last Report of the International Committee on Atomic Weights.

Thomsen maintained his interest in thermochemical problems up to the end, and was a keen and clear-sighted critic of the work which appeared from time to time during the later years of his life. This interest occasionally gave rise to controversy, and some of his latest papers were wholly polemical.

Thomsen was a pronounced atomist, and to him a chemical process was a change in the internal structure of a molecule, and the chief aim of chemistry was to investigate the laws which control the union of atoms and molecules during the chemical process. He considered that chemistry should be treated mathematically as a branch of rational mechanics. But no one insisted more strongly than he how little we really know of these questions. In summarising his theoretical ideas in the *Thermokemiske Resultater*, he says, "An almost impenetrable darkness hides from us the inner structure of molecules and the true nature of atoms. We know only the relative number of atoms within the molecule, their mass, and the existence of certain groups of atoms or radicles in the molecule, but with regard to the forces acting within the molecules and causing their formation or destruction our knowledge is still exceedingly limited." He fully realised that his own work was only the foundation on which the future elucidation of these questions must rest. "He worked," says Brönsted, "in the conviction that what we somewhat vaguely call the affinity of the atoms—their interaction, their attraction, and varying effect, etc.—follows the general laws of mechanics, and that, as he worded it, the principle that 'might is right,' holds good in chemistry as in mechanics. On this foundation he hoped to be able to evolve the laws for the statics and dynamics of chemical phenomena, even although the true nature of the action is unknown."

Thomsen's merits as an investigator received formal recognition from nearly every country in the civilised world. As far back as 1860 he was elected one of the thirty-five members of the Danish Royal Society of Sciences of Copenhagen, and from 1888 until his death he was its President. In 1876 he became an Honorary Foreign Member of the Chemical Society of London. On the occasion of the fourth centenary of the foundation of the University of Upsala (created in 1477), he received the degree of Doctor of Philosophy *honoris causa*. In 1879 he was made an honorary M.D. of the University of Copenhagen. Two years later he was made a

Foreign Member of the Physiographical Society of Lund, and in 1838 he was elected a member of the Society of Science and Literature of Gothenburg. In 1835 he became a member of the Royal Society of Sciences of Upsala, and in 1836 of the Stockholm Academy of Sciences.

In 1833 he and Berthelot were together awarded the Davy Medal of the Royal Society—a fitting and impartial recognition on the part of the Society of the manner in which the two investigators, whose work not infrequently brought them into active opposition, had jointly and severally contributed to lay the foundations of thermochemistry.

In the same year Thomsen was made a member of the Accademia dei Lincei of Rome, and in the following year he was elected into the American Academy of Arts and Sciences in Boston, and of the Royal Academy of Sciences of Turin. In 1837 he was made a member of the Royal Belgian Academy.

In 1836-37 and again in 1891-92 he was Rector of the University of Copenhagen. In 1838 he became Commander of the Dannebrog, and in 1896, and on his seventieth birthday, he was made Grand Commander of the same order. On the same occasion the Danish chemists caused a gold medal to be struck in his honour. In 1902 he became a Privy Counsellor (Geheime Konferenz raad). In the same year he was elected a Foreign Member of the Royal Society of London.

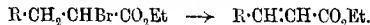
He died on February 13th, 1903, full of years as of honours, and was buried on the eighty-third anniversary of his birth and on the jubilee of the opening of the Oeresund factory. His wife, Elmine Hansen—the daughter of a farmer on Langeland—predeceased him in 1890.

I desire to express my acknowledgments to Director G. A. Hagemann, of Copenhagen, and to Professor Arrhenius, of Stockholm, for their assistance in obtaining information concerning Thomsen's personal history. I am also much indebted to our Fellow, Mr. Harald Faber, for his kindness in making for me a translation of Professor Brönsted's account of Thomsen's scientific work, on which my own résumé is mainly based.

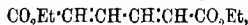
XVIII. Formation of Heterocyclic Compounds. Part II. Action of Bases on the $\alpha\alpha$ -Dibromo-derivatives of Certain Dicarboxylic Acids.

By HENRY RONDEL LE SUEUR and PAUL HAAS.

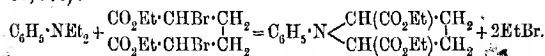
THE action of diethylaniline on aliphatic compounds containing bromine, and more especially on the esters of α -bromo-monocarboxylic acids (Crossley and Le Sueur, *Trans.*, 1899, 75, 161; 1900, 77, 83), is to remove the elements of hydrogen bromide with the formation of the corresponding unsaturated compound:



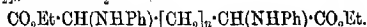
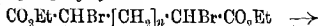
This action has been regarded as quite a general one, and holds good in the majority of instances. In the case of ethyl $\alpha\alpha$ -dibromoadipate, $CO_2Et \cdot CHBr \cdot [CH_2]_2 \cdot CHBr \cdot CO_2Et$, a compound in which the two bromine atoms are separated from each other by four carbon atoms, the action of diethylaniline is quite different. Here it is true small quantities of the unsaturated ester, ethyl muconate,



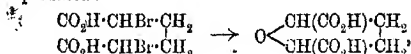
are formed, but by far the main product of the reaction is ethyl 1-phenylpyrrolidine-2:5-dicarboxylate (Le Sueur, *Trans.*, 1900, 95, 276):



This reaction involves the fission of the two ethyl groups in diethylaniline, a change which is generally not easily effected, but that this actually takes place was proved by the isolation and identification of large quantities of ethyl bromide resulting from the above reaction. The action of aniline is quite similar to that of diethylaniline, as is shown by the action of aniline on methyl $\alpha\alpha$ -dibromoadipate when the corresponding pyrrolidine ester is produced. The usual action of aniline on compounds of this type is to replace the bromine atom by the group $C_6H_5 \cdot NH$:

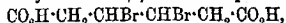


This great tendency for the formation of a five-membered ring is further illustrated by the action of alcoholic potassium hydroxide on $\alpha\alpha$ -dibromoadipic acid, whereby *cis*-tetrahydrofuran-2:5-dicarboxylic acid is produced:



the usual action of alcoholic potassium hydroxide, namely, the removal of hydrogen bromide and formation of the corresponding unsaturated compound, only taking place to a small extent, as only small quantities of muconic acid were obtained.

In contrast to the above reaction, we may compare the action of alcoholic potassium hydroxide on β -dibromoadipic acid,

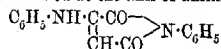


whereby Rupe (*Annalen*, 1890, 256, 1) obtained an 85 per cent. yield of muconic acid. In the bromo-acid employed by Rupe, the two bromine atoms are attached to adjacent carbon atoms, and there is therefore no possibility of the formation of a five-membered ring, and so the action is the normal one. The constitution of muconic acid was discussed by Rupe, who concluded that it is correctly expressed by the formula $\text{CO}_2\text{H}\cdot\text{CH}:\text{CH}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$; this conclusion is fully confirmed by the facts that the acid is obtained from $\alpha\delta$ -dibromoadipic acid and the ethyl ester from ethyl $\alpha\delta$ -dibromoadipate as described in the present communication.

In order to ascertain if cyclic compounds analogous to ethyl 1-phenylpyrrolidine-2:5-dicarboxylate would be obtained from the corresponding bromo-derivatives of other dicarboxylic acids, the action of aniline and monoethylaniline on these bromo-derivatives was investigated.

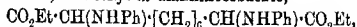
The action of aniline on ethyl $\alpha\beta$ -dibromosuccinate has been already studied by Gorodetzky and Hell (*Ber.*, 1888, 21, 1796), who obtained ethyl $\alpha\beta$ -dianilinosuccinate, $\text{CO}_2\text{Et}\cdot\text{CH}(\text{NHPh})\cdot\text{CH}(\text{NHPh})\cdot\text{CO}_2\text{Et}$, as the main product, together with a small quantity of a yellow compound which they were unable to identify. It was thought that this yellow substance might be the desired cyclic compound containing the ring

system $\text{C}_6\text{H}_5\cdot\text{N}\begin{smallmatrix} \diagup \text{C} \\ \diagdown \text{C} \end{smallmatrix}$, but this was found not to be the case, and the compound was identified as the anil of anilinomaleic acid,



(Bischoff and Walden, *Annalen*, 1894, 279, 139).

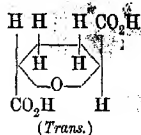
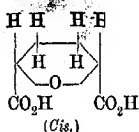
The action of monoethylaniline on ethyl $\alpha\beta$ -dibromosuccinate was next investigated, and in this case the compound obtained was ethyl bromomaleate, $\text{CO}_2\text{Et}\cdot\text{CBr}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, which was obtained in a 74.2 per cent. yield. Ethyl $\alpha\beta$ -dibromosebacate was then substituted for ethyl $\alpha\beta$ -dibromosuccinate, and heated with aniline, when it was found that no cyclic compound had been formed, but that the action had followed the normal course, and ethyl $\alpha\beta$ -dianilinosuccinate,



was obtained.

By heating an aqueous solution of the lactone of dihydroxybutane-

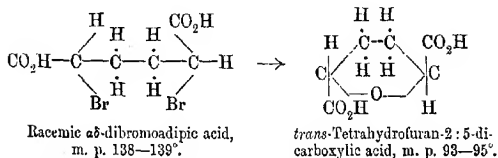
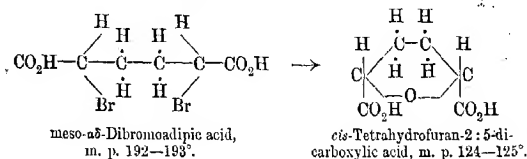
tetracarboxylic acid, Lean (Trans., 1900, 77, 110) obtained two isomeric tetrahydrofuran-2:5-dicarboxylic acids, which he regarded as *cis*- and *trans*-modifications:



One of these acids melted at 123–125°, and the other, which melted at 93–95°, formed a hydrate melting at 63–64°, but Lean did not establish which of these acids was the *cis*- and which the *trans*-variety.

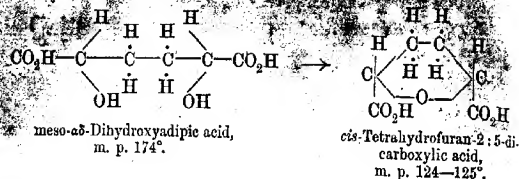
In a former communication (Le Sueur, Trans., 1908, 93, 716), the preparation and identification of two $\alpha\delta$ -dihydroxyadipic acids were described, and it was shown that the $\alpha\delta$ -dihydroxyadipic acid melting at 174° is the *meso*-acid, and the one melting at 146° is the racemic variety. Corresponding with these two hydroxyadipic acids are two $\alpha\delta$ -dibromoadipic acids; of these, the one melting at 192–193° is the *meso*-acid, and the other, which melts at 138–139°, is the racemic acid (compare Rosenlew, Ber., 1904, 37, 2090).

Now, when *meso*- $\alpha\delta$ -dibromoadipic acid is treated with alcoholic potash, the tetrahydrofuran-2:5-dicarboxylic acid obtained is the one melting at 124–125°, and from stereochemical considerations it will be seen that this must be the *cis*-variety:



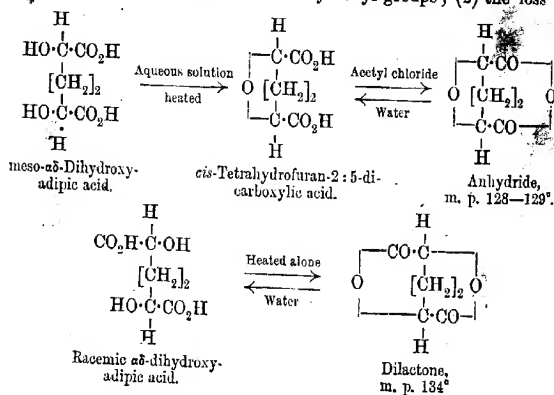
It might be argued that the *meso*-dibromoadipic acid under such severe treatment as the action of boiling alcoholic potash had undergone intramolecular change, and that the acid resulting from it was the *trans*- and not the *cis*-form. In order to settle this point,

an aqueous solution of the meso- $\alpha\delta$ -dihydroxyadipic acid was heated in a sealed tube, when the acid lost a molecule of water and gave the tetrahydrofuran-2:5-dicarboxylic acid melting at 124—125°:



Finally, if the furan acid melting at 124—125° is really the *cis*-acid, then it should form an anhydride, whereas the *trans*-acid would not. In order to investigate this point, the acid melting at 124—125° was boiled for several hours with an excess of acetyl chloride, when an anhydride, $\text{C}_6\text{H}_6\text{O}_4$, was obtained. This anhydride, on treatment with water, readily regenerated the acid melting at 124—125°, which proves conclusively that the acetyl chloride has not caused an intramolecular change, and that the anhydride really corresponds with the tetrahydrofuran-2:5-dicarboxylic acid melting at 124—125°, which latter acid must therefore be regarded as the *cis*-modification.

It is interesting to note that the above anhydride is isomeric with the dilactone obtained by heating racemic $\alpha\delta$ -dihydroxyadipic acid (Trans., 1908, 93, 721). Both the anhydride and the dilactone are formed by the loss of two molecules of water from their respective dihydroxyadipic acids, the former being formed in two stages: (1) the loss of a molecule of water from two hydroxyl groups; (2) the loss of



a second molecule of water from two carboxyl groups, whereas the dilactone is formed by the loss of two molecules of water, each molecule of water arising from one hydroxyl group and one carboxyl group.

EXPERIMENTAL.

Action of Diethylaniline on Ethyl $\alpha\delta$ -Dibromoadipate.

Ten grams of ethyl $\alpha\delta$ -dibromoadipate (m. p. 66°) and 16 grams of recently distilled diethylaniline were placed together in a flask attached to a reflux air condenser and containing a thermometer, the upper end of the condenser being connected to a U-tube immersed in a freezing mixture. The flask and contents were gradually heated to 190° , at which temperature the reaction began, and were maintained at 185 – 195° for three hours. During the heating a volatile liquid was evolved, and was condensed in the U-tube; the total amount of ester heated in this manner was 80 grams.

The volatile liquid, after being dried, weighed 15 grams, and boiled at 38 – 38.5° :

0.1544 gave 0.2644 AgBr. Br = 72.87.

C_8H_9Br requires Br = 73.39 per cent.

The liquid was therefore ethyl bromide, the boiling point of which is 38.37° .

The contents of the flask partly solidified on cooling, and were added to dilute hydrochloric acid and the whole extracted with ether; the ethereal solution was washed, dried, and evaporated, and the residue distilled under 29 mm. pressure:

165–185°	11.5 grams	230–255°	11.0 grams
210–223°	3.0 „	Undistilled residue...	13.5 „

The fraction b. p. 165 – 185° slowly deposited long, flat crystals, which, after filtration and drying, weighed 3.3 grams, and, after crystallisation from light petroleum (b. p. 40 – 60°), melted at 63 – 64° , and consisted of ethyl muconate, the melting point of which is quoted as 63 – 64° by Rubemann and Blackman (Trans., 1890, 57, 374):—

0.1760 gave 0.3892 CO_2 and 0.1148 H_2O . C = 60.31; H = 7.24.

$C_{10}H_{11}O_4$ requires C = 60.60; H = 7.07 per cent.

The fraction b. p. 230 – 255° consisted for the most part of ethyl 1-phenylpyrrolidine-2:5-dicarboxylate, as was shown by the fact that it yielded 1-phenylpyrrolidine-2:5-dicarboxylic acid on hydrolysis with 10 per cent. alcoholic potash. The acid which was precipitated on acidifying the hydrolysed product with hydrochloric acid was crystallised from a mixture of acetone and light petroleum, from which it separated in oblong plates, which decomposed with evolution of gas at 249° . A mixture of equal parts of this substance and 1-phenyl-

pyrrolidine-2:5-dicarboxylic acid (Trans., 1909, 95, 277) decomposed at the same temperature.

0.1684 gave 8.6 c.c. N_2 (moist) at 18° and 764 mm. $N = 6.97$.

$C_{12}H_{16}O_4N$ requires $N = 6.96$ per cent.

The undistilled residue consisted of a dark thick syrup, which, after being kept for several months, showed no signs of solidifying, and from which no pure substance could be isolated.

Action of Aniline on Methyl $\alpha\delta$ -Dibromoadipate.

Eighteen grams of methyl $\alpha\delta$ -dibromoadipate and 18 grams of aniline were heated together in a flask immersed in boiling water for forty hours, and the product worked up and distilled as described under the action of diethylaniline on ethyl $\alpha\delta$ -dibromoadipate (p. 177). That portion of the distillate boiling at $225-230^\circ/32$ mm. weighed 8 grams, and solidified on cooling. It was crystallised from light petroleum, when it was obtained in needles, which melted at 88° and had all the properties of methyl 1-phenylpyrrolidine-2:5-dicarboxylate (Trans., 1909, 95, 277). A mixture of equal parts of these two substances melted at 88° . When hydrolysed by boiling with 10 per cent. alcoholic potash, it gave 1-phenylpyrrolidine-2:5-dicarboxylic acid, which decomposed and evolved gas at 252° .

Action of Monoethylaniline on Ethyl $\alpha\beta$ -Dibromosuccinate.

The ethyl dibromosuccinate was prepared by heating succinic acid with amorphous phosphorus and bromine in a sealed tube and esterifying the resulting bromo-acid with concentrated sulphuric acid and alcohol (Gorodetzky and Hell, *Ber.*, 1888, 21, 1729).

Twenty grams (1 mol.) of ethyl $\alpha\beta$ -dibromosuccinate and 15 grams (2 mols.) of monoethylaniline were heated together in boiling water for thirty-five hours; the resulting product, which partly solidified on cooling, was extracted with much ether, and the insoluble residue of monoethylaniline hydrobromide filtered off. The ethereal filtrate was well washed with water, dried, and evaporated, and the residue distilled under 32 mm. pressure, when the whole distilled between 149° and 152° . It was re-distilled, and a portion boiling at $148-149^\circ$ collected for analysis:

0.2125 gave 0.2981 CO_2 and 0.0838 H_2O . $C = 38.26$; $H = 4.38$.

0.1854 " 0.1400 AgBr. $Br = 32.13$.

$C_8H_{11}O_4Br$ requires $C = 38.24$; $H = 4.38$; $Br = 31.87$ per cent.

The above substance is therefore ethyl monobromomaleate, the boiling point of which is given as $143^\circ/30-40$ mm. (Anschütz, *Ber.*, 1879, 12, 2284).

Twenty grams of ethyl dibromosuccinate gave 11.2 grams of the pure ester, which corresponds with 74.2 per cent. of the theoretical, so that this reaction affords a very convenient method for preparing ethyl monobromosuccinate.

The interaction of monoethylaniline and ethyl $\alpha\beta$ -dibromosuccinate was tried under various conditions, such as heating together the two substances in alcoholic solution; heating together at 180–200°, but in all cases ethyl monobromosuccinate was the only substance obtained.

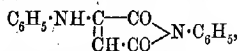
Action of Aniline on Ethyl $\alpha\beta$ -Dibromosuccinate.

Ten grams of ethyl $\alpha\beta$ -dibromosuccinate (1 mol.) and 14 grams (5 mols.) of aniline were heated together for two hours in a flask immersed in boiling water. The contents of the flask partly solidified on cooling, and were treated with a large volume of ether and the crystalline solid collected. This solid, which consisted chiefly of aniline hydrobromide, was treated with 80 c.c. of warm water, the solution cooled, and the undissolved residue (0.8 gram) collected and crystallised from alcohol, when it was obtained in glistening needles, which melted at 149° and had all the properties of ethyl $\alpha\beta$ -dianilinosuccinate, the melting point of which is given as 150° by Gorodetzky and Helf (*Ber.*, 1888, 21, 1797).

The ethereal filtrate, on evaporation, left a residue which showed signs of decomposition on attempting to distil it under diminished pressure; it was therefore not distilled, but alcohol was added to it when a yellow solid slowly separated. This solid was repeatedly crystallised, first from acetone and finally from a mixture of chloroform and light petroleum, when it was obtained in small needles melting at 230°:

0.1224 gave 10.8 c.c. N_2 (moist) at 18.5° and 769 mm. $N = 10.29$.
 $C_{16}H_{12}O_2N_2$ requires $N = 10.60$ per cent.

This yellow solid is insoluble in ether, light petroleum, or alcohol, and moderately soluble in boiling chloroform or acetone; it is, therefore identical with the anilino-maleic anil,



obtained by Bischoff and Walden (*loc. cit.*).

The yield of the above yellow solid was very small, and many attempts were made to increase it, but without any substantial improvement. Among these attempts may be mentioned: (1) addition of anhydrous sodium acetate to the mixture of ester and aniline; (2) the substitution of aniline hydrochloride for aniline; (3) the

interaction of the ester and aniline in alcoholic solution in the cold; (4) the interaction of the ester and aniline in the presence of potassium hydroxide; (5) heating the ester and aniline at 190°.

Action of Aniline on Ethyl $\alpha\beta$ -Dibromosebacate.

The ethyl $\alpha\beta$ -dibromosebacate was prepared by the action of bromine on the acid chloride of sebacic acid, and esterification of the resulting bromo-acid chloride by the interaction of this substance and alcohol.

Twenty grams (1 mol.) of ethyl $\alpha\beta$ -dibromosebacate and 20 grams (4 mols.) of recently distilled aniline were heated together for eleven hours in a flask immersed in boiling water. The resulting solid was triturated with dilute hydrochloric acid, and the undissolved solid (4.5 grams) collected and washed with water. The hydrochloric acid solution was diluted with a large volume of water, when a solid was precipitated; the whole was extracted with ether, the ethereal solution washed, dried, and evaporated, when 12.5 grams of solid residue were obtained. This was added to the above 4.5 grams of undissolved residue, and recrystallised from alcohol until the melting point was constant:

0.1304 gave 7.5 c.c. N_2 (moist) at 18.5° and 756 mm. $N = 6.58$.

$C_{20}H_{30}O_4N_2$ requires $N = 6.36$ per cent.

Ethyl $\alpha\beta$ -dianilino-sebacate,

$CO_2Et \cdot CH(NHPh) \cdot [CH_2]_6 \cdot CH(NHPh) \cdot CO_2Et$,
melts at 119.5—120.5°, and crystallises from alcohol in fern-like aggregates. It is insoluble in water, sparingly soluble in ether, alcohol, or light petroleum, and readily so in chloroform, benzene, or acetone.

The alcoholic mother liquors from which the above ester had crystallised gave a substance which, after recrystallisation, melted at 94—100°, and on analysis gave the following results:

0.1680 gave 0.4378 CO_2 and 0.1342 H_2O . $C = 71.07$; $H = 8.87$.

0.1734 „ 9.7 c.c. N_2 (moist) at 16° and 764 mm. $N = 6.55$.

$C_{26}H_{30}O_4N_2$ requires $C = 70.90$; $H = 8.18$; $N = 6.36$ per cent.

This substance is therefore in all probability stereoisomeric with the ethyl $\alpha\beta$ -dianilino-sebacate melting at 119.5—120.5°, but repeated recrystallisation failed to give a substance with a definite melting point.

$\alpha\beta$ -Dianilino-sebacic Acid.—Thirty-three grams of ethyl $\alpha\beta$ -dianilino-sebacate were added to a solution of 20 grams of potassium hydroxide in 150 c.c. of alcohol containing a few c.c. of water, and the whole boiled for five hours. The resulting solution was concentrated to half its volume, and gradually added to a boiling solution of 25 c.c. con-

centrated sulphuric acid in 125 c.c. of water, when the anilino acid was precipitated in a granular form. If the precipitation is carried out in the cold, then the acid separates in an amorphous form, in which condition it is difficult to manipulate. The acid was collected, washed with water, dried, and boiled with 80 c.c. of alcohol in order to remove any non-hydrolysed ester, filtered, and after drying weighed 23 grams. It was crystallised from amyl alcohol, from which it separated in spherical aggregates of small needles, which melt and evolve gas at 210—213°:

0.1254 gave 0.3180 CO_2 and 0.0868 H_2O . $\text{C} = 69.15$; $\text{H} = 7.69$.

0.1707 „ 10.6 c.c. N_2 (moist) at 18° and 765 mm. $\text{N} = 7.21$.

$\text{C}_{22}\text{H}_{28}\text{O}_4\text{N}_2$ requires $\text{C} = 68.75$; $\text{H} = 7.29$; $\text{N} = 7.29$ per cent.

ab-Diamilinosebacic acid,



is insoluble in water, alcohol, ether, chloroform, light petroleum, benzene, or ethyl acetate, and only sparingly soluble in boiling amyl alcohol.

The silver salt was obtained as a white precipitate on adding a solution of the sodium salt of the acid to a solution of silver nitrate; it darkened somewhat readily on drying:

0.1510 gave 0.0536 Ag. $\text{Ag} = 35.5$.

$\text{C}_{22}\text{H}_{26}\text{O}_4\text{N}_2\text{Ag}_2$ requires $\text{Ag} = 36.1$ per cent.

Methyl ab-diamilinosebacate,



was prepared by the interaction of aniline and methyl *ab*-dibromosebacate, as described for the preparation of the corresponding ethyl ester. It is insoluble in water, ether, or light petroleum, readily soluble in benzene or chloroform, and crystallises from alcohol, in which it is sparingly soluble, in fern-like aggregates of needles melting at 133—136°:

0.1334 gave 7.9 c.c. N_2 (moist) at 19° and 768 mm. $\text{N} = 6.88$

$\text{C}_{24}\text{H}_{32}\text{O}_4\text{N}_2$ requires $\text{N} = 6.79$ per cent.

Action of Alcoholic Potassium Hydroxide on meso-ab-Dibromoadipic Acid.

The meso-*ab*-dibromoadipic acid was separated from the mixture of racemic and meso-*ab*-dibromoadipic acids obtained by the action of bromine on the acid chloride of adipic acid (Trans., 1908, 93, 718) by extracting the mixed acids with water and crystallising the insoluble residue of the meso-acid from formic acid until its melting point was constant (Rosenlew, Ber., 1904, 37, 2090).

Seven and a-half grams of meso-*ab*-dibromoadipic acid (m. p.

192—193°) were dissolved in 15 c.c. of hot alcohol, and the hot solution gradually added to a boiling solution of 10.5 grams of potassium hydroxide in 60 c.c. of alcohol. A vigorous reaction immediately set in, and the mixture was boiled on the water-bath for fifteen minutes, then allowed to cool, and filtered (filtrate = A). The insoluble residue was dissolved in 15 c.c. of water, the solution strongly acidified with concentrated hydrochloric acid, and, after some time, a crystalline precipitate separated; this was collected and dissolved in dilute potassium hydroxide solution, and again precipitated by hydrochloric acid, when it was obtained in a crystalline form. The substance had all the properties of muconic acid, and decomposed without melting at 272°:

0.1608 gave 0.2966 CO_2 and 0.0678 H_2O . $\text{C} = 50.30$; $\text{H} = 4.68$.

$\text{C}_6\text{H}_8\text{O}_4$ requires $\text{C} = 50.70$; $\text{H} = 4.22$ per cent.

The aqueous filtrate from the muconic acid was evaporated to a small bulk, and repeatedly extracted with a large volume of ether. The ethereal solution was evaporated without previous washing or drying, and the residue dried and crystallised from a mixture of ethyl acetate and light petroleum, when it was obtained in nodular aggregates melting at 124—125°:

0.1434 gave 0.2344 CO_2 and 0.0684 H_2O . $\text{C} = 44.58$; $\text{H} = 5.30$.

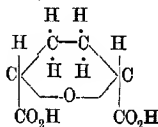
$\text{C}_6\text{H}_8\text{O}_5$ requires $\text{C} = 45.00$; $\text{H} = 5.00$ per cent.

The molecular weight was determined by dissolving the acid in water and titrating with $N/10$ -sodium hydroxide, using phenolphthalein as indicator:

0.2040 required 25.6 c.c. $N/10$ - NaOH , which corresponds with a dibasic acid of $\text{M.W.} = 159.4$.

A dibasic acid, $\text{C}_6\text{H}_8\text{O}_5$, requires $\text{M.W.} = 160$.

The substance is therefore *cis*-tetrahydrofuran-2:5-dicarboxylic acid,



It readily chars, when heated above its melting point, and its solubilities in various solvents correspond exactly with those of the tetrahydrofuran-2:5-dicarboxylic acid melting at 123—125° obtained by Léan (*loc. cit.*).

The alcoholic filtrate A (see above) was saturated with carbon dioxide, and the precipitated potassium hydrogen carbonate collected. The filtrate was evaporated to dryness, the residue dissolved in a very

small quantity of water, and the resulting solution acidified with hydrochloric acid and repeatedly extracted with a large volume of ether. The ethereal solution on evaporation left a small residue, which, after crystallisation from ethyl acetate and light petroleum, melted at 174° and had all the properties of meso-2,3-dihydroxyadipic acid, *Trans.*, 1908, 93, 723).

The aqueous mother liquors from the ether extracts were mixed and evaporated to dryness; the residue obtained was dried, extracted with alcohol, and the alcoholic solution evaporated and the residue crystallised from ethyl acetate and light petroleum, when a further small quantity of the tetrahydrofuran acid melting at $124-125^{\circ}$ was obtained.

The amount of tetrahydrofuran acid obtained corresponded with 28 per cent. of the theoretical, and the yield of muconic acid was only 14 per cent. of the theoretical.

The ammonium salt was prepared by dissolving the acid in alcohol and saturating the solution with ammonia, when the salt was precipitated; it was collected, and crystallised by dissolving in a small quantity of water and adding alcohol and ether, when it separated out in long, transparent prisms. It is readily soluble in water, sparingly so in alcohol, and insoluble in ether:

0.1231, boiled with NaOH, gave 0.0213 NH_3 . $N = 14.24$.

$\text{C}_6\text{H}_8\text{O}_5(\text{NH}_4)_2$ requires $N = 14.43$ per cent.

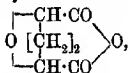
Anhydride of cis-Tetrahydrofuran-2:5-dicarboxylic Acid.

Twenty grams of acetyl chloride and 2.8 grams of *cis*-tetrahydrofuran-2:5-dicarboxylic acid were boiled together for sixteen hours in a flask attached to a reflux condenser. The acetyl chloride was removed by evaporation in a vacuum over 50 per cent. potassium hydroxide solution, and the resulting solid spread on a porous plate, when 2.5 grams of solid, melting at $97-105^{\circ}$, were obtained. This, on extraction with 15 c.c. of dry chloroform, left 1.5 grams of residue which melted at 122° , and consisted of the unchanged acid. The chloroform extract, on evaporation in a vacuum, gave 0.6 gram of a solid, which was crystallised from dry chloroform and light petroleum, when it was obtained in slender needles:

0.1022 gave 0.1876 CO_2 and 0.0414 H_2O . $C = 50.1$; $H = 4.5$.

$\text{C}_6\text{H}_4\text{O}_4$ requires $C = 50.7$; $H = 4.2$ per cent.

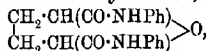
The *anhydride of cis-tetrahydrofuran-2:5-dicarboxylic acid*,



readily volatilises when heated, even on the water-bath, and yields a

sublimate of long needles, which melt at 128—129°. It is readily soluble in ethyl acetate, chloroform, ether, or acetone in the cold, and is insoluble in light petroleum. It slowly dissolves in cold water, giving a strongly acid solution, which on evaporation gives the original *cis*-tetrahydrofuran-2:5-dicarboxylic acid melting at 124—125°. When the anhydride is heated with resorcinol and a few drops of sulphuric acid, and the product poured into a solution of potassium hydroxide, a green, fluorescent solution is obtained.

cis-Tetrahydrofuran-2:5-dicarboxyldianilide,



was prepared by boiling the acid (0.2 gram) with a large excess of aniline (2 grams) for seven hours. The product was poured into dilute hydrochloric acid, and the precipitated solid collected, dissolved in alcohol, and the solution decolorised by animal charcoal. The solid which separated out on cooling was crystallised from alcohol, when it was obtained in small, thick plates, melting and decomposing at 208—209°. The dianilide is readily soluble in acetone or chloroform in the cold, sparingly soluble in hot benzene or cold alcohol, and insoluble in water:

0.1176 gave 9.4 c.c. N_2 (moist) at 12° and 766 mm. $\text{N} = 9.51$.

$\text{C}_{18}\text{H}_{18}\text{O}_8\text{N}_2$ requires $\text{N} = 9.03$ per cent.

Formation of cis-Tetrahydrofuran-2:5-dicarboxylic Acid from meso-αδ-Dihydroxyadipic Acid.

One gram of *meso-αδ*-dihydroxyadipic acid (m. p. 174°), obtained by hydrolysis of the *meso-αδ*-dibromoadipic acid melting at 192—193° (Trans., 1908, 93, 719), was dissolved in 5 c.c. of water, and the solution heated in a sealed tube for three hours at 200°. The solution was filtered to remove a small quantity of black solid, and the filtrate repeatedly extracted with a large volume of ether. The ethereal solution on evaporation left 0.2 gram of solid which, after drying and crystallisation from ethyl acetate and light petroleum, melted at 124—125°; this melting point was unaltered by mixing the substance with an equal quantity of *cis*-tetrahydrofuran-2:5-dicarboxylic acid. The substance readily charred when heated above its melting point, and its solubilities in various solvents were identical with those of the *cis*-furan acid.

Action of Alcoholic Potassium Hydroxide on Racemic αδ-Dibromoadipic Acid

The action of alcoholic potassium hydroxide on the racemic *αδ*-dibromoadipic acid (m. p. 138—139°) was investigated in the hope

of obtaining the *trans*-tetrahydrofuran-2,5-dicarboxylic acid. The method of procedure was exactly as described for the action of alcoholic potassium hydroxide on the meso-dibromoadipic acid, and muconic acid and a trace of the *cis*-tetrahydrofuran acid were obtained, together with a small quantity of residue which could not be crystallised. No such residue was obtained from the action of alcoholic potassium hydroxide on the meso-dibromoadipic acid, and it is not improbable that this residue did contain some of the *trans*-tetrahydrofuran acid, which, on account of its solubility and reluctance to crystallise (Lean, *loc. cit.*), could not be isolated.

CHEMICAL LABORATORY,
ST. THOMAS'S HOSPITAL,
LONDON, S.E.

XIX.—*The Half-life Period of Radium; a Correction.*

By ROBERT WHYTLAW GRAY and SIR WILLIAM RAMSAY, K.C.B.

IN making the calculation of the half-life period of radium in the paper which has recently appeared (Trans., 1909, 95, 1082), an error, which Mr. Soddy was so good as to point out to us, was made inadvertently. Half the reciprocal of the disintegration-constant of radium, equal to half the average life-period, was given as the period of half-decay, namely, 1258 years. The true half-life period should have been calculated from the equation: $R = R_0 e^{-\lambda t}$, where R is the initial amount of radium, R_0 the quantity remaining after half has decayed, e the base of natural logarithms, λ the disintegration-constant for radium (the reciprocal of which is the average life-period), and t the time in years.

To find λ from the equilibrium-quantity, N_0 , of emanation per gram of radium, the volume of which was 0.601 cub. mm., the amount of emanation given off per second was calculated by means of the equation: $q_0 = \lambda N_0 = \frac{0.601}{481,000} = 1.25 \times 10^{-6}$ cubic millimetres per second; the fraction $1/481,000$ is the value of λ , the disintegration constant for the emanation, calculated from the half-life period of 3.86 days. This volume is equal to the diminution in volume of 1 gram of radium per second, supposing it to be a monatomic gas.

Hence the fraction of the total quantity of radium changed per second is 1.25×10^{-6} of the volume of 1 gram of gaseous radium.

This is equal to $\frac{1.25 \times 10^{-6} \times 226}{22,400 \times 1000}$, 226 being the accepted atomic

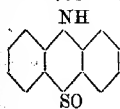
weight for radium; the expression is equivalent to $1/2516$ per year, and is Λ , or the disintegration-constant for radium. In decimals, it is 3.98×10^{-4} gram per year; hence the half-life period for radium is 1744 years, or, in other words, 1 gram of radium will have been reduced to 0.5 gram after 1744 years.

UNIVERSITY COLLEGE,
LONDON.

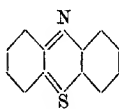
XX.—The Intramolecular Rearrangement of Diphenylamine ortho-Sulphoxides. Part II.

By EDWARD DE BARRY BARNETT and SAMUEL SMILES.

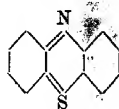
In a previous communication to the Society on this subject it was shown that the ortho-sulphoxides of diphenylamine (type I) may be transformed by the action of acid reagents into the sulphonium hydrates (type II). At the same time it was observed that if the



(I.)



(II.)



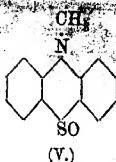
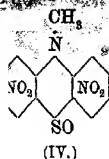
(III.)

sulphonium grouping be sufficiently basic, the corresponding salt (type III) may be formed. The tetranitro- and the two isomeric dinitro-sulphoxides yielded the sulphonium hydrates, but the parent compound (I) furnished phenazothionium chloride. In the four cases examined, it was observed that the sulphonium derivatives contain an additional molecule of water; but usually this may be removed by crystallisation from high boiling solvents.

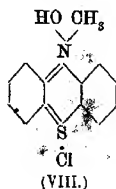
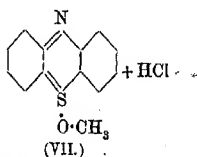
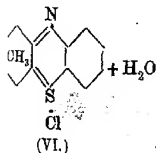
The investigation of this reaction has been continued with the object of determining the mechanism by which the change takes place, and the results are now collected in the following pages.

From the mere inspection of the formulae (I and II) representing the initial and final products of the reaction, it might be supposed that the sulphonium hydrate is formed simply by the migration of hydrogen from the imino-group to the oxygen of the thionyl group. In order to test whether this is actually the case or not, we have examined the behaviour of sulphoxides in which this imino hydrogen is replaced by alkyl. It has been found that these derivatives undergo the change as readily as the unsubstituted compounds. The two chief examples studied were the dinitro-*N*-methyldiphenylamine ortho-sulphoxide (IV), which has been pre-

viously obtained by Bernthsen from the nitration of *N*-methylthiodiphenylamine, and the *N*-methylthiodiphenylamine sulphoxide (V), which we have prepared by oxidation of the sulphide.



Assuming that the course of the reaction is the same with these *N*-alkyl derivatives as with the imino-compounds, it might then be concluded that with the latter the reaction does not involve the direct movement of the imino-hydrogen atom, for on a priori grounds it is improbable that the alkyl group should be transferred with such ease under the conditions favourable to the reaction. This conclusion, however, cannot be accepted until some actual proof is obtained of the immobility of the alkyl group, for many instances are known where the transposition of alkyl from one atom to another can be detected, although the treatment then required is usually more energetic than that necessary to the present reaction. The proof that alkyl is not removed from nitrogen during the reaction has been obtained in the case of *N*-methylthiodiphenylamine *o*-sulphoxide. This sulphoxide, when treated with hydrogen chloride, absorbs one molecular proportion of the halogen acid, being then converted into the chloride of a base which is deep red in colour and has properties similar to those of the phenazothionium derivatives described in a previous paper. It may be remarked that the quinonoid structure of this chloride is demonstrated by the further action of hydrochloric acid, which yields a chloro-derivative of *N*-methylthiodiphenylamine. If the methyl group is transferred from the nitrogen in this reaction, the only alternatives are that it may either enter the aromatic nucleus (as in VI), or become attached to the thionyl group (as in VII). In either case the substance which is formed would be represented as follows VI and VII):



and on reduction it should furnish either a methylthiodiphenylamine (from VI) or thiodiphenylamine itself (from VII). We find, however, that reduction of the quinonoid salt does not yield either of these compounds, but that instead *N*-methylthiodiphenylamine is formed. It follows that the constitution of this substance must be as represented in the third of the foregoing (VIII) formula; but it is impossible conclusively to show whether salt formation takes place at the ammonium or sulphonium groups. Moreover, the salt is not very stable, since, as previously noticed, it readily changes to chloro-*N*-methylthiodiphenylamine, thus affording further proof of the immobility of the methyl group. The experiments dealing with these derivatives of *N*-methylthiodiphenylamine are described in the following paragraphs.

EXPERIMENTAL

Conversion of N-Methyldiphenylamine ortho-Sulphoxide into the Sulphonium Derivative.

Attempts to prepare this sulphoxide were made by treating *N*-methylthiodiphenylamine with hydrogen dioxide in acetone solution, but only small quantities of the substance could be obtained by this method, almost the whole of the sulphide being recovered unchanged after remaining with the reagent for about three weeks. Attention is drawn to this result, since thiodiphenylamine is readily oxidised to the sulphoxide under these conditions. Berntsen (*Annalen*, 1885, **230**, 92) has shown that *N*-methylthiodiphenylamine may be converted into the sulphone by hot aqueous permanganate, but we find that this reagent under similar conditions furnishes satisfactory yields of the sulphoxide.

A solution of six grams of *N*-methylthiodiphenylamine in acetone was acidified with dilute sulphuric acid, more acetone being added, if necessary, to retain all in solution. Two grams of finely powdered potassium permanganate were then gradually added, the temperature being kept at about 15° by immersing the flask in cold water. Care was taken to ensure the presence of a slight excess of sulphuric acid during the reaction. The mixture was shaken for a few hours; then the crystalline precipitate was collected, and well washed with water. The residue was agitated with a cold aqueous solution of sulphurous acid, and finally recrystallised from alcohol. The least soluble portion contained small quantities of the sulphone, and it was therefore rejected. Nine grams of the crude sulphoxide were obtained from 13 of sulphide.

N-Methyldiphenylamine ortho-sulphoxide forms colourless leaflets, which melt at 193°. It is sparingly soluble in cold acetone or

alcohol, and insoluble in water. Concentrated sulphuric or hydrochloric acid forms bright red solutions, which contain the phenazonium derivative. A sample which had been dried in a vacuum was analysed:

0.1009 gave 0.2520 CO_2 and 0.0443 H_2O . $\text{C}=67.9$; $\text{H}=4.88$.

0.2315 „ 12.6 c.c. N_2 at 17° and 763 mm. $\text{N}=6.4$.

$\text{C}_{13}\text{H}_{11}\text{ONS}$ requires $\text{C}=68.1$; $\text{H}=4.8$; $\text{N}=6.3$ per cent.

Action of Acids.—This sulphoxide is readily soluble in concentrated aqueous hydrochloric acid, being then converted into the deep crimson hydrochloride. The attempts made to isolate the latter in the pure condition were unsuccessful, chiefly on account of the hygroscopic nature of the substance, and the ease with which it is transformed into the chloro-derivative of *N*-methylthiodiphenylamine. The platinichloride was therefore prepared by addition of chloroplatinic acid to the aqueous solution of the salt. The precipitate was collected, and after recrystallisation it was dried in a vacuum before analysis:

0.2161 gave 0.0474 Pt. $\text{Pt}=21.93$.

0.1184 „ 0.1568 CO_2 and 0.0238 H_2O . $\text{C}=36.1$; $\text{H}=2.2$.

$(\text{C}_{13}\text{H}_{11}\text{ONS}, \text{HCl})_2\text{PtCl}_4$ requires $\text{Pt}=22.4$; $\text{C}=35.9$.

$\text{H}=2.7$ per cent.

The *platinichloride* of *N*-methylphenazonium (VIII) forms minute, reddish-brown needles, which melt with profound decomposition at about 255° .

Reduction.—The hydrochloride was reduced as rapidly as possible in methyl-alcoholic solution with tin and hydrochloric acid. When reduction was complete, the colourless solution was poured into water, and the precipitate was collected. The product contained a small quantity of the chloro-derivative, and, in order to remove this, it was fractionally crystallised from methyl alcohol. The melting point and solubility of the chloro-compound lie close to those of *N*-methylthiodiphenylamine, and a complete separation is not easily made. However, after repeated crystallisation, a sample, which melted at 98° , was obtained, and this, when mixed with *N*-methylthiodiphenylamine (m. p. 100°), melted at the same temperature. It contained traces of chlorine. In order to obtain further proof that thiodiphenylamine is not formed during the reduction of the chloride, both the crude and purified (m. p. 98°) products of reduction were treated with nitric acid (D 1.4) under the conditions which yield the dinitro-derivatives of the group. The nitro-derivative was insoluble in hot aqueous alkali hydroxide, whereas the nitro-derivatives of thiodiphenylamine are readily attacked by this reagent, yielding deep red solutions of the alkali

salts. Experiments made with artificial mixtures showed that very small quantities of thioldiphenylamine may be detected in the presence of a large excess of the *N*-methyl derivative by this method. These experiments show that the methyl group of *N*-methylthiodiphenylamine remains undisturbed during the conversion to the quinonoid salt.

Conversion of N-Methyldinitrophenylamine o-Sulphoxide.—The dinitro-sulphoxide was prepared from *N*-methylthiodiphenylamine by the action of nitric acid, and it was purified in the manner recommended by Bernthsen (*Annalen*, 1885, 230, 92). To ensure the purity of the substance employed, a sample was analysed:

0.1037 gave 0.1841 CO₂ and 0.0298 H₂O. C=48.4; H=3.2.

C₁₃H₉O₅N₃S requires C=48.9; H=2.8 per cent.

The conversion of the sulphoxide into the sulphonium derivative was effected by means of sulphuric or hydrochloric acid.

(a) *Concentrated Sulphuric Acid.*—A solution of dinitro-*N*-methylthiodiphenylamine *o*-sulphoxide in this acid was set aside for half an hour at the atmospheric temperature, and then poured on to powdered ice. The solid precipitate was collected and washed with water until free from sulphuric acid; it was then triturated with dilute aqueous sodium hydroxide to remove a small quantity of soluble material. The latter is probably formed by replacement of the nitro- by the hydroxyl group (see Barnett and Smiles, *Trans.*, 1909, 95, 1262), but it was not further investigated. After renewed filtration and washing, the reddish-brown product was crystallised from hot glacial acetic acid. Samples of the once (1) and four times recrystallised (2) product were analysed after being dried in the steam-oven.

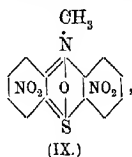
(b) *Hydrogen Chloride.*—Methyl alcohol was saturated with gaseous hydrogen chloride at 0°, and excess of the solution was mixed with the dinitro-sulphoxide. The mixture was shaken for six hours, and then set aside at the atmospheric temperature. After the lapse of forty-eight hours, the dark brown liquid contained in suspension an orange-red, crystalline substance, and, since this evidently was different from the more soluble portion, it was collected and separately treated. The solution, which was shown by subsequent experiment to contain the bulk of the desired sulphonium compound, was mixed with a large quantity of water, and the now insoluble product was collected and purified by recrystallisation from glacial acetic acid. Analysis (3) was then made with a sample from the fourth recrystallisation. The crude product contained traces of non-ionisable halogen:

- (1) 0.1010 gave 0.1774 CO₂ and 0.0296 H₂O. C=47.9; H=3.26.
- (2) 0.1005 „ 0.1752 CO₂ „ 0.0266 H₂O. C=47.5; H=2.87.
- (3) 0.1006 „ 0.1752 CO₂ „ 0.0287 H₂O. C=47.5; H=3.16.

C₁₃H₉O₃N₂S₂H₂O requires C=47.56; H=3.0 per cent.

The analyses show that, as with the nitro-derivatives of thio-diphenylamine which have been previously studied (Trans., 1909, 95, 1257), the conversion of the sulphoxide to the sulphonium derivative is accompanied by absorption of water; but here the molecular proportion is half that previously observed, and it is more firmly retained, since it cannot be removed by heating or by recrystallisation from high boiling solvents.

Dinitro-N-methylphenazothionium hydrate forms reddish-brown leaflets, which do not melt below 250°. It is sparingly soluble in cold benzene or glacial acetic acid. By reduction and subsequent oxidation, the substance is converted into the greenish-blue dye which is obtained by the same process from the dinitro-sulphoxide; but in contrast with the latter it does not exhibit the reaction characteristic of the thionyl group (Trans., 1906, 89, 696), since it does not yield the *S*-phenetyl derivative when treated with phenetole and sulphuric acid. The only formula which can be assigned to the anhydrous compound is the following:



but from reasons which will presently be stated, it is probable that the additional water in these substances is of constitution.

The insoluble portion of the product which was obtained by the action of hydrochloric acid on the dinitro-sulphoxide was separately collected and recrystallised from hot glacial acetic acid. It was thus obtained in bright orange-red leaflets, which remained undecomposed at 250°. Samples from two different preparations were analysed:

- (1) 0.1004 gave 0.1777 CO₂ and 0.0303 H₂O. C=48.3; H=3.51.
- (2) 0.2028 „ 0.3616 CO₂ „ 0.0516 H₂O. C=48.6; H=2.8.

C₁₃H₉O₃N₂S requires C=48.90; H=2.82 per cent.

When crystallised from hot nitrobenzene, the substance is obtained with solvent of crystallisation:

0.2000 gave 0.3718 CO₂ and 0.0656 H₂O. C=50.7; H=3.6.

2C₁₃H₉O₃N₂S.C₆H₅O₂N requires C=50.6; H=3.0 per cent.

The presence of nitrobenzene in this substance was proved by mixing the sulphuric acid solution with water and passing a current of steam through the liquid. The substance melts and decomposes at about 280°. Further experiment showed that this compound does not contain the sulphonium grouping, and since it yields the *S*-phenetylsulphonium salt when treated with phenetole in sulphuric acid solution, it may for the present be regarded as an isomeric form of the original sulfoxide. Probably the isomerism involves the nitro-grouping.

Assuming that the conversion of sulfoxide (I) to sulphonium base (II) takes place in the same manner with the imino-compounds as with these *N*-methyl derivatives, it is clear that the hypothesis of migration of hydrogen from the imino- to the thionyl group cannot be accepted as an adequate explanation of the change. The ortho-sulfoxides of diphenylamine contain the imino- and thionyl groups, and it is well known that each of these in simple derivatives possesses basic properties. So far as the thionyl group is concerned, it has been shown that the aliphatic (Saytzeff, *Annalen*, 1867, 144, 148) and aromatic (Smiles and Le Rossignol, *Trans.*, 1906, 89, 697) sulfoxides form nitrates and hydrochlorides. From these considerations and from the fact that the reaction can be effected only by acid reagents, it seems probable that the salts of the sulfoxides are formed in an initial stage of the reaction, and that these are subsequently changed into the sulphonium derivatives. That a causal relation exists between the formation of these salts and the production of the sulphonium compounds may be shown by the following experiments.

(1) *The Action of the same Acid Reagent on Sulfoxides of Varying Basic Power.*—Experiments were made with the tetra-nitro-, di-*p*-nitro-, isodinitro-, and the unsubstituted diphenylamine sulfoxides, the reagent being alcohol saturated with hydrogen chloride at the atmospheric temperature. In each case the conditions adopted were the same: the sulfoxide was shaken with a large excess of the acid reagent at about 15–17°, and the approximate time required for the complete conversion to the sulphonium was observed. The results are collected in the following table:

Substance.	Approximate time required.
Diphenylamine <i>o</i> -sulfoxide.....	apparently instantaneous.
<i>N</i> -Methyldiphenylamine <i>o</i> -sulfoxide.....	apparently instantaneous.
Di- <i>p</i> -nitrodiphenylamine <i>o</i> -sulfoxide.....	about five hours.
isoDinitrodiphenylamine <i>o</i> -sulfoxide.....	about five hours.
Tetra-nitrodiphenylamine <i>o</i> -sulfoxide ...	about three weeks.

The data cannot be regarded as anything more than very rough approximations; but they serve to show that by decreasing the

basic function of the sulphoxides, the tendency to form the sulphonium base is correspondingly diminished.

(2) *The Action of Acids of Varying Strength on the same Sulphoxide.*—In these experiments the diphenylamine *o*-sulphoxide was employed as the standard. The colourless solutions of this substance become deeply coloured on the addition of acids, the salt of phenazothionium being then formed. Equal volumes (50 c.c.) of 2*N*-aqueous solutions of acetic, monochloroacetic, trichloroacetic, and hydrochloric acids were separately mixed at the same moment with 50 c.c. of an alcoholic solution (0.1 per cent.) of the sulphoxide. After a suitable lapse of time (thirty minutes), the solutions were examined in layers of equal depth. A difference between the intensity of colour in these solutions could be readily detected, but quantitative measurements of the intensity were not made, since the solutions containing the stronger acids were of slightly different colour, probably owing to the formation of di-acid salts. When arranged in order of increasing intensity of colour, the solutions fall into the following order:

Fifty c.c. of 0.1 per cent. Solution of Diphenylamine Sulphoxide in Alcohol.

With 50 c.c. of 2 <i>N</i> -solution of	Relative coefficients of saponification velocity.	Remarks.
Acetic acid	0.003	colour appeared after 1 hour.
Monochloroacetic acid	0.043	faint colour immediately produced.
Trichloroacetic acid	0.632	immediate coloration.
Hydrochloric acid	1.000	immediate coloration.

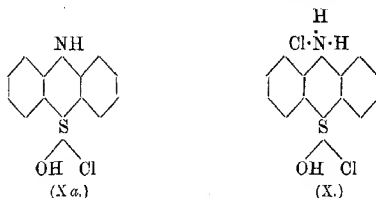
It may be remarked that after the further lapse of time the intensity of colour in these solutions increases, and the difference between each solution becomes even more pronounced. The centre column of the table shows the relative affinities of the acids; the data were obtained by Ostwald (*J. pr. Chem.*, 1883, [ii], 28, 449) from measurements of the velocity of hydrolysis of methyl acetate.

Assuming that the intensity of colour of these solutions is roughly proportionate to the quantity of azothionium salt present, it follows that the amount of this salt formed at the end of a given period is controlled by the strength of the acid employed. It is clear that these two sets of experiments justify the hypothesis that the conversion of the sulphoxides to the sulphonium compounds depends on the preliminary formation of salts of the former substances with the acid reagent.

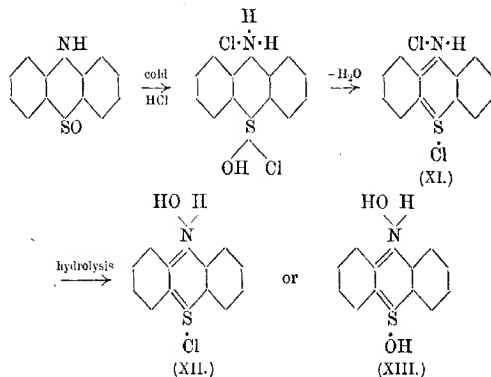
It is, however, difficult conclusively to determine the process by which these salts are converted to the quinonoid compounds, since they cannot be isolated in the pure condition for separate treat-

ment. There are, however, only two alternatives: either (a) that they lose the elements of water, or (b) that migration of hydroxyl takes place. These will be separately dealt with in the order given.

To assume that elimination of water takes place in the mono-acid sulphoxide salt (Xa) is evidently incorrect, for on this basis the conversion of the *N*-methyl derivative would be impossible, and no account would be forthcoming of the additional molecule of water in the products. In all the examples studied, a large excess of acid is necessary completely to effect the reaction, and this fact lends colour to the assumption that the salts which undergo the change are of the di-acid type (X). It is apparent that these



salts would be converted into the azothionium salts by the loss of the elements of water, the complete process being represented as follows:

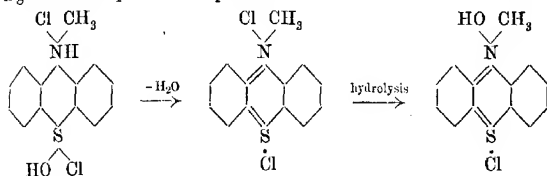


Moreover, it is apparent that whether the resulting quinonoid salt (XI) can be isolated or not must depend on the basic character of the sulphonium and ammonium groups, and this is controlled by the nature and number of the groups present in the aromatic

nuclei (Kehrmann, *Ber.*, 1906, **39**, 914; Smiles and Hilditch, *Trans.*, 1908, **93**, 1691). For example, the parent phenazothionium compound is obtained as the monohalide (XII) (*Trans.*, 1909, **95**, 1259), whilst the di- and tetra-nitro-derivatives, being completely hydrolysed during the process of isolation, appear as sulphonium hydrates (XIII).

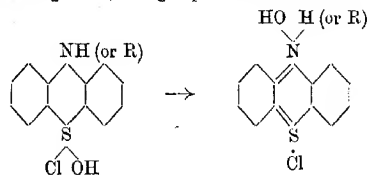
It is necessary to observe that this explanation of the process satisfactorily accounts for the invariable occurrence in the azothionium compounds of an additional molecule of water, which is so difficult to remove as to give rise to the suspicion that it is not merely water of crystallisation.

Moreover, a satisfactory account is given of the conversion of the *N*-methyl sulfoxide to the sulphonium compound. The following formulæ represent the process:



In this case it must remain doubtful whether hydrolysis takes place at the ammonium or sulphonium group, but the formula given for the product is the more probable of the two alternatives, for with the parent compound there can be no doubt that the product is the sulphonium halide, since it has been isolated in the anhydrous condition (Kehrmann, *Ber.*, 1901, **34**, 4170).

The alternative hypothesis of migration of hydroxyl from quadrivalent sulphur to trivalent nitrogen in the sulfoxide salt affords an equally satisfactory explanation of the change. From this point of view the reaction must be regarded as a true intramolecular rearrangement, being represented as follows:



But, as previously remarked, we are at present unable to offer any decisive evidence for the preference of either alternative hypothesis. On general grounds, the former of the alternatives given seems the more probable.

In conclusion, it must be stated that the hypothesis described is advanced to account for the following facts:

(1) The immobility of the alkyl group during the conversion of *N*-methyldiphenylamine *o*-sulphoxide.

(2) The more basic the character of the sulphoxide, the more readily does the change take place with a given acid reagent.

(3) The conversion of a given sulphoxide proceeds more easily the stronger the acid employed.

(4) The absorption of the elements of water during the reaction.

The results of the study of this reaction may be summed up as follows:

(1) The conversion of diphenylamine sulphoxides to phenazothionium derivatives does not take place by direct migration of hydrogen from the imino-group to the oxygen of the thionyl group.

(2) The salts of the imino-sulphoxides are first formed with the acid reagent, and these are then converted into the phenazothionium salt either (a) by loss of the elements of water, or (b) by migration of hydroxyl from the quadrivalent sulphur to tervalent nitrogen.

Preliminary experiments have shown that the conversion of the thionyl group to the quinonoid thionium arrangement may be effected not only in other cyclic systems, but also in hydroxy- and amino-sulphoxides. These substances are now being investigated.

In conclusion, we desire to thank the Research Fund Committee of the Chemical Society for a grant which has defrayed the expense of this research.

THE ORGANIC CHEMISTRY LABORATORY,
UNIVERSITY COLLEGE, LONDON.

XXI.—*The Adsorption of Uranium-X by Barium Sulphate.*

By ARTHUR JOHN BERRY, B.A.

BEQUEREL has shown (*Compt. rend.*, 1900, 131, 137; 1901, 133, 977) that when barium is precipitated as sulphate in a uranium solution, the photographic activity of the latter is removed by the barium sulphate. A similar result was obtained by Sir William Crookes (*Proc. Roy. Soc.*, 1900, 66, 409), who found that uranium compounds could be obtained photographically inactive by a single chemical operation, the whole of the photographic activity being concentrated in a small residue termed uranium-X by Crookes. Soddy (*Trans.*, 1902, 81, 860) showed that the whole of the β -ray

activity of uranium is due to the uranium-X, which is one of the disintegration products of uranium (Rutherford and Soddy, *Phil. Mag.*, 1903, [vi], 5, 441).

In the present communication, the adsorption of uranium-X has been investigated quantitatively, and evidence has been obtained of a definite "partition coefficient" between the uranium-X in the barium sulphate and in the solution. As the experiments were approaching completion, the author's attention was directed to a paper by Ritzel (*Zeitsch. physikal. Chem.*, 1909, 67, 724). Ritzel investigated the absorption of uranium-X by carbon, and he mentions (*loc. cit.*, p. 727): "Als Adsorbens wollte ich zunächst Bariumsulfat verwenden. Vorversuche zeigten aber bald, dass das Bariumsulfat, von Versuch zu Versuch, mit sehr schwankender Kristallgrösse ausfällt, und man kann deshalb keine guten Resultate erhalten." The present writer did not experience any difficulty of that kind. It was usually found perfectly easy to repeat a result under any given conditions. However, the use of barium sulphate is a disadvantage in studying the effect of time in the adsorption of uranium-X, as it is probable that the crystals would increase in size with lapse of time.

EXPERIMENTAL.

A solution of pure uranyl nitrate (Merck), containing 400 grams per litre, was employed. This solution was in radioactive equilibrium. Experiments were always carried out with 25 c.c. of this solution. The β -ray activity due to the uranium-X in this quantity of material was determined by Crookes's original method (*loc. cit.*). The liquid was diluted considerably, heated to boiling, a trace of ferric chloride added, and ammonium carbonate added in quantity sufficient to redissolve the precipitate of uranium carbonate. The liquid was then filtered from the ferric hydroxide, and the activity of the uranium-X, removed by the latter, measured by a β -ray electroscope.

This electroscope was of the ordinary single-leaf type. The case of the instrument was a stout brass cylinder, the internal diameter being 10.1 cm., and the internal height 12.6 cm. The base of the electroscope was of aluminium foil 0.1 mm. thick. The preparations were placed on a board at a fixed distance (7.7 cm.) below the base of the instrument. The rate of leak was determined in the usual way with a reading microscope and a stop-watch. In every case, the "natural leak" of the instrument was determined and allowed for. This natural leak varied but slightly, the usual value being 3.7 scale divisions per minute. The measurements were always compared with the leak due to a standard consisting of black

uranium oxide. The mean of three concordant determinations of the β -ray activity in 10 grams of uranyl nitrate carried out in this manner was 106.6 scale divisions per minute.

It was always possible to separate more than 90 per cent. of the uranium- X in the first operation by Crookes's method. On acidifying the filtrate with nitric acid, and repeating the process, practically all the remaining uranium- X was removed. This was checked by testing the residue after ignition.

Unless otherwise stated, the experiments were conducted as follows. The measured quantity of uranyl nitrate solution was taken, acidified with a given quantity of a 10 per cent. solution of sulphuric acid, and a quantity of water added, which, together with the quantity of standard barium nitrate (2.5 grams per litre) employed for precipitation, would make the solution up to some definite volume. The precipitation was carried out in the cold, and the liquid kept overnight. The solution was then boiled for one minute, the barium sulphate collected, and its β -ray activity measured. The absorption of the β -radiation in the barium sulphate may be neglected, since the greatest mass of precipitate on the filter paper was only 0.11 gram.

If there is a definite equilibrium between the uranium- X in the barium sulphate and in the liquid, we should have:

$$\frac{C_{\text{BaSO}_4}}{C_{\text{liquid}}} = k,$$

where C is the concentration of the uranium- X , and k and n are constants. The concentration in the barium sulphate is x/m , where x is the amount of uranium- X adsorbed, and m the mass of barium sulphate. The concentration in the liquid is $a-x/v$, where a is the initial quantity of uranium- X and v is the volume of the solution. If there is equilibrium we should have:

$$\frac{\log(a-x)}{\log \frac{x}{m}} = \frac{1}{n} = \text{constant.}$$

Series I.— $a=106.6$ divisions per minute. 1 c.c. of 10 per cent. sulphuric acid added to liquid. $v=150$ c.c.

m (gram).	x (divisions per minute).	$\frac{\log(a-x)}{\log \frac{x}{m}} = \frac{1}{n}$
0.0044	2.7	0.74
0.0088	5.3	0.72
0.0110	6.3	0.73
0.0154	8.1	0.73
0.033	14.7	0.74
0.044	19.3	0.74
0.066	21.8	0.77
0.088	24.1	0.78

Series II.— $a=106.6$ divisions per minute. 10 c.c. of 10 per cent. sulphuric acid added to liquid. $v=250$ c.c.

m (gram).	x (divisions per minute).	$\frac{\log(a-x)}{\log \frac{x}{m}} = \frac{1}{n}$
0.0044	4.1	0.68
0.0110	15.1	0.63
0.022	38.7	0.57
0.033	47.7	0.56
0.044	54.7	0.56
0.055	60.3	0.55
0.088	70.3	0.54
0.110	76.9	0.52

Series III.—In this series the procedure was somewhat different. The uranium-X from one quantity (25 c.c.) of uranyl nitrate was removed by successive precipitations on separate days. The filtrates were always made up to a constant volume (140 c.c.), and precipitated each day by 10 c.c. of the solution of barium nitrate; 15 c.c. of 10 per cent. sulphuric acid were added at the beginning of the series only. $v=150$ c.c. In calculating $1/n$, a correction was made for the value of $(a-x)$, owing to the solution recovering its uranium-X content with time. The correction was made by a recovery curve for uranium-X. $m=0.022$ gram. a (initially)=106.6 divisions per minute.

x (divisions per minute).	$(a-x)$ (corrected for recovery of Ur.-X).	$\frac{\log(a-x) \text{ (corrected)}}{\log \frac{x}{m}} = \frac{1}{n}$
43.7	64.6	0.55
30.4	35.8	0.50
17.3	21.0	0.46
10.0	13.7	0.43
5.6	11.0	0.43

Series IV.—This series is precisely similar to series III, excepting that 20 c.c. of 10 per cent. sulphuric acid were added to start with. $v=150$ c.c., $m=0.022$ gram, and a (initially)=106.6 divisions per minute.

x (divisions per minute).	$(a-x)$ (corrected for recovery of Ur.-X).	$\frac{\log(a-x) \text{ (corrected)}}{\log \frac{x}{m}} = \frac{1}{n}$
45.0	63.0	0.54
30.4	34.7	0.49
17.0	20.1	0.45
8.7	13.9	0.44
5.6	11.2	0.44

From series I and II, it is evident that dilution and excess of sulphuric acid favour the adsorption of uranium-X, other things being equal. The influence of these two factors, separately, was confirmed by numerous other experiments, which it is unnecessary to describe here.

Series III and IV are of interest, inasmuch as continually diminishing the concentration of the uranium-X in the solution scarcely affects the constancy of $1/\eta$.

With regard to the effect of time, the following experimental facts may be of interest. It was found that as much uranium-X was adsorbed by the barium sulphate two hours after precipitation as when the liquid was kept all night after precipitation. But if the liquid was kept for three days before collecting the barium sulphate, the quantity of uranium-X adsorbed was greater. This would appear to indicate that adsorption takes place very rapidly at first, but that diffusion of the uranium-X into the barium sulphate particles takes place afterwards, and this latter process goes on for a considerable time. However, no great importance is to be attached to these time experiments, owing to the probable increase in size of the adsorbing particles. For the same reason, it is difficult to obtain evidence as to whether there is a definite equilibrium between the uranium-X in the solid and liquid phases which can be approached from both sides. Such a reversible equilibrium has been shown to exist in the case of the partition of uranium-X between carbon and solution by Ritzel (*loc. cit.*, p. 735); who finds that for this equilibrium the equation $C_l = \text{constant} \times C_k$, where C_l and C_k denote the concentration of the uranium-X in the solution and in the carbon respectively.

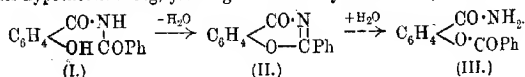
The author desires to express his sincere thanks to Mr. Soddy for the interest he has taken in these experiments and for his valuable suggestions.

PHYSICAL CHEMISTRY LABORATORY,
GLASGOW UNIVERSITY.

XXII.—2-Phenyl-1:3-benzoxazine-4-one.

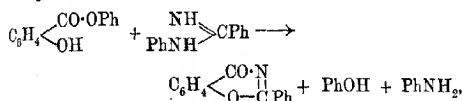
By ARTHUR WALSH TITHERLEY.

IN his criticism of the metoxazone theory of labile isomerism in the acylsalicylamide group, Auwers (*Ber.*, 1907, **40**, 3506) attributed the change of *N*-benzoylsalicylamide (I) to *O*-benzoylsalicylamide (III) (by boiling with acetic acid) to the intermediate formation of the unsaturated ring (II) by loss of water, which then immediately decomposed this hypothetical ring, yielding the *O*-benzoyl derivative, thus:



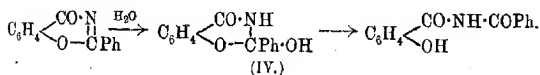
This view was shown to be untenable by Titherley and Hicks (Trans., 1909, 95, 908), but it appeared desirable to effect if possible the synthesis of this ring-compound in order that a study of its properties might be made in relation to the derivatives in the acyl-salicylamide group. Several attempts were made to prepare it from phenylbenzometoxazone,* $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{C} \cdot \text{HPh} \end{smallmatrix}$, by eliminating two hydrogen atoms, and from *O*- and *N*-benzoylsalicylamides by the action of dehydrating agents, like phosphoric oxide and zinc chloride, but without success.

Eventually the compound was synthesised from phenyl salicylate and phenylbenzamidine by loss of phenol and aniline, thus:



and it was later found that the same ring-compound could be obtained when special precautions were observed, by the action of hydrogen chloride on either *N*- or *O*-benzoylsalicylamide at temperatures between 110° and 140°. These independent syntheses, which are discussed later, and the properties of the compound place its constitution beyond doubt, and it is, therefore, 2-phenyl-1:3-benzoxazine-4-one.

The compound has the same melting point, 106°, as that of its isomeride, benzoylsalicylnitrile, $\text{CN} \cdot \text{C}_6\text{H}_4 \cdot \text{OBz}$, from which, however, it differs greatly. It is markedly additive in properties, and its most striking addition is with water. With pure water or dilute alkalis it is almost unaffected, but in presence of hydrogen ions it rapidly adds one molecule of water, a quantitative yield of *N*-benzoylsalicylamide being produced. This simple circumstance finally disposes of Auwers's hypothetical contention which involves direct hydrolytic rupture at the double linking, but is intelligible on the author's theory that the intermediate hydroxy-derivative (IV) is too unstable to exist, as already frequently indicated, and at once rearranges to *N*-benzoylsalicylamide, thus:

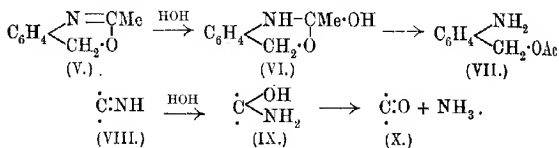


The still alternative explanation that hydrolytic rupture takes place

* The correct name of this compound is 2-phenyldihydro-1:3-benzoxazine-4-one but in view of its use in previous papers, "phenylbenzometoxazone" is retained in the present one.

between the phenolic oxygen atom and the carbon atom to which the phenyl group is attached, is discounted by the comparatively great stability of the unsaturated ring-compound with alkali, which would favour such a rupture, and the only possible mechanism appears to be the above, which is identical with that occurring in the conversion of nitriles into amides through the agency of acids.

The above mechanism throws some light upon the decomposition by water in presence of hydrogen ions of certain allied compounds in which the double linked C:N pair appears in the molecule. Auwers observed (*Ber.*, 1904, 37, 2249) that the comparatively stable unsaturated ring (V) yields a hydrobromide which in aqueous solution adds water and passes into the salt of *o*-aminobenzyl acetate (VII), whilst J. F. Thorpe has shown that all true imino-compounds (VIII) are at once decomposed by dilute acids, giving ketonic derivatives (X). In these cases a similar mechanism is evidently at work, in which (1) the hydroxyl group attaches itself to carbon and the hydrogen atom to nitrogen, and (2) the resulting unstable compound (VI or IX) changes either by wandering of a hydrogen atom or by loss of ammonia into a stable derivative:



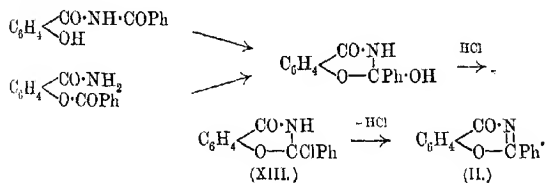
That such intermediate hydroxy-compounds are first formed in the cases observed by Auwers and Thorpe appears to follow from the complete analogy of these reactions to that of 2-phenyl-1:3-benzoxazine-4-one, where the production of the intermediate hydroxy-compound must be admitted on the grounds already stated and in view of the author's previous observations.

Contrasting the intermediate hydroxy-derivatives in the author's case (XI) with that of Auwers (XII):



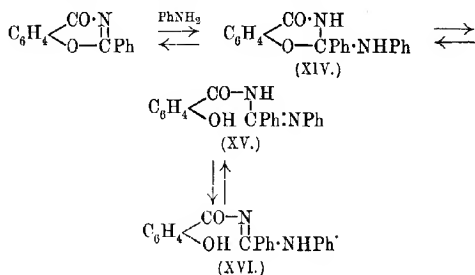
it is clear that when the hydrogen atom of the hydroxyl group wanders, (XI) yields an *N*-acyl derivative, whilst (XII) yields an *O*-acyl derivative. Theoretically, each could yield an *O*- or *N*-acyl derivative according to whether the hydrogen atom wandered to nitrogen or to the phenolic oxygen atom, and the final result probably depends on the conditions which favour one or other of these alternatives. Thus, in Auwers's case it is natural that the hydro-

bromic acid would favour the production of the *O*-acyl derivative, which is a base and yielded the salt, rather than the neutral *N*-acyl derivative, which is an amide. In the author's case neither the *O*- nor *N*-benzoylsalicylamide is a base, and the rearrangement yields simply the stable form (*N*-benzoyl). At the same time it must be noted that, although neither of the isomerides is a base in the ordinary sense, *O*-benzoylsalicylamide as a primary amide must be more basic than its isomeride, which is secondary. Experiments which have been made on the two isomerides show that the former is more basic, and yields a definite hydrochloride when treated in presence of benzene with hydrogen chloride. It might therefore be anticipated that hydrogen chloride should effect the rearrangement of *N*-benzoylsalicylamide into its isomeride [through the hydroxy-form (XI)]. Such a change has already been partly effected by continued boiling with pure acetic acid (McConnan and Titherley, *Trans.*, 1906, 89, 1331), a fact which supports the supposition that the intermediate hydroxy-form may open in either of the two alternative ways according to conditions (acetic acid favouring the production of the more basic *O*-benzoyl derivative). Experiments on the action of hydrogen chloride on *N*-benzoylsalicylamide in benzene showed that no change took place in the cold, but that in presence of boiling xylene slow and incomplete rearrangement to *O*-benzoylsalicylamide occurred. As the experiments proceeded, however, it became apparent that, besides rearrangement, chemical elimination of water was taking place at about 130°. By using ethylene dibromide or anisole as solvents and distilling off the water as produced, the latter action was accelerated, and 2-phenyl-1:3-benzoxazine-4-one was formed in large quantities. The latter was even more easily obtained by the action of hydrogen chloride on *O*-benzoylsalicylamide in boiling toluene or xylene if the water formed was continually removed. The hydrogen chloride virtually behaves as a catalyst, since relatively small quantities were found to be sufficient to effect the change. It is probable that the loss of water is not due to direct dehydration, but to the intermediate formation of the chloro-derivative (XIII), which immediately loses hydrogen chloride and apparently is incapable of existence:



When 2-phenyl-1:3-benzoxazine-4-one (II) in benzene solution is treated with dry hydrogen chloride, a white, crystalline compound containing chlorine is precipitated, which on exposure to atmospheric moisture rapidly passes into *N*-benzoylsalicylamide, but on treatment with aniline yields a yellow, crystalline solid, melting at 106°, which was found to have the constitution $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{N}\cdot\text{CPh}\cdot\text{NHPh}$ (salicylphenylbenzamidine). From this behaviour it was supposed that the ring-compound had added hydrogen chloride, giving the chloro-compound (XIII), or, by rearrangement, the compound $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{N}\cdot\text{CClPh}$, either of which might be expected to behave as above with water and aniline (see below). But from the fact that the hydrogen chloride additive product in presence of benzene regenerates the original ring-compound (II) with alkali, and from its other properties, it must be concluded that the product is merely the salt, $\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{N}\cdot\text{HCl}$, which with water would at once give *N*-benzoyl-

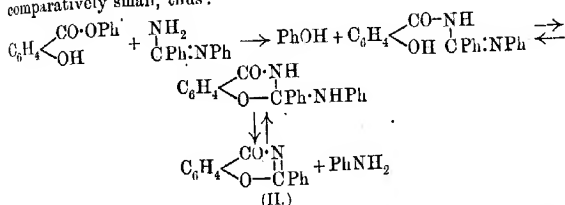
salicylamide (as explained above); whilst its curious behaviour with aniline subsequently became clear when it was found that the free ring-compound itself readily unites with aniline, producing the above amidine derivative according to the following scheme:



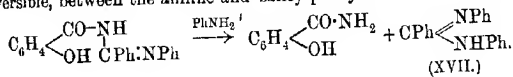
The reaction is reversible, and the anilino-derivative (salicylphenylbenzamidine) is a tautomeric substance. Its tautomerism comprises the three forms (XIV), (XV), and (XVI), of which the last two represent ordinary amidine tautomerism, and it is evident that one of these two formulæ must be given to the substance itself, melting at 106°, because of its phenolic properties. It loses aniline, however, below 100°, and passes quantitatively into 2-phenyl-1:3-benzoxazine-4-one, provided that the aniline is removed, and the easy reversibility of the above process would seem to imply that the compound is bordering on the verge of ring-formation (XIV). That the phenolic hydroxyl group and the group $\cdot\text{CPh}\cdot\text{NHPh}$ are in intimate steric association is confirmed by the difficulty with which the substance

dissolves in dilute aqueous sodium hydroxide, and at first it was supposed that the ring formula (XIV) must be adopted for the substance. This view, however, is inconsistent with the bright yellow colour of the substance, for whilst phenylbenzometoxazone and 2-phenyl-1:3-benzoxazine-4-one are colourless, the alkali and ammonia derivatives of *N*-acetylsalicylamides are bright yellow, and the phenolic nature of the anilino-derivative is confirmed by the strong ferric chloride reaction it gives.

In the synthesis of 2-phenyl-1:3-benzoxazine-4-one by heating phenyl salicylate with phenylbenzamidine, this anilino-compound is the first product of the reaction, and it is owing to its reversible decomposition, as above, that the unsaturated ring compound (II) is obtained, and for the same reason the yield of the latter is comparatively small, thus:



A considerable quantity of diphenylbenzamidine (XVII) is also produced as a result of a secondary reaction, which also appears to be reversible, between the aniline and salicylphenylbenzamidine, thus:



EXPERIMENTAL.

2-Phenyl-1:3-benzoxazine-4-one.

(a) *Preparation from Phenyl Salicylate*:—(a) 21.4 Grams of phenyl salicylate and 19.6 grams of phenylbenzamidine were heated at 110° for six and a-half hours, during which aniline and phenol were produced in quantity. On cooling, the resulting viscid, yellow syrup was stirred with 150 c.c. of water and 100 c.c. of 10 per cent. sodium hydroxide to remove phenol and salicylphenylbenzamidine, and the yellow alkaline solution was decanted off. The remaining syrup was washed with water, dissolved in 200 c.c. of pure benzene, and the benzene solution washed with alkali and water. In order to remove aniline and diphenylbenzamidine, the benzene solution was shaken for a few minutes with about 300 c.c. of 5 per cent. sulphuric acid, the upper benzene solution washed with water, and then as rapidly as possible

shaken with dilute alkali, to remove the *N*-benzoysalicylamide formed during washing with acid and to neutralise the remaining traces of acid. (During the former operation some loss was entailed, because of the great instability of the ring compound* in presence of dilute acid.)

The alkali extract was found to contain besides phenol, a considerable quantity of salicylphenylbenzamidine, which was precipitated on adding acid and then decomposed, giving *N*-benzoysalicylamide. The acid extract contained aniline and diphenylbenzamidine. The latter was isolated (4 grams), and found to be identical with Wallach's compound (*Annalen*, 1877, 184, 83).

The clear benzene solution was washed twice with water, dried, and evaporated at about 40°. Massive crystals remained, together with a syrupy portion, which crystallised after several hours. After washing with a little ether and draining on porous porcelain, the crude product (12.5 grams) was crystallised from 700 c.c. of light petroleum, the solution being allowed to cool very slowly to avoid deposition of syrup. White or transparent, colourless leaflets or plates (m. p. 104°; 10.5 grams) separated, which on recrystallisation from light petroleum were obtained in the pure state and then melted sharply at 106–107°:

0.2193 gave 0.6024 CO₂ and 0.0759 H₂O. C = 74.92; H = 3.85.

0.1688 „ 9.3 c.c. N₂ (moist) at 20° and 757 mm. N = 6.28.

0.3480, by Kjeldahl's method, required 16.0 c.c. *N*/10-HCl. N = 6.39.

C₁₄H₉O₂N requires C = 75.34; H = 4.03; N = 6.27 per cent.

2-Phenyl-1:3-benzoxazine-4-one is very soluble in chloroform or acetone, readily so in benzene, methyl alcohol, or ethyl acetate, and rather less so in ethyl alcohol, ether, or pyridine. It dissolves in about 70 parts of light petroleum (b. p. 90–120°). It may be recovered unchanged after solution in these solvents, even pyridine. Its solutions give no coloration with alcoholic ferric chloride. In glacial acetic acid it readily dissolves, but owing to the presence of moisture the solution soon deposits *N*-benzoysalicylamide.

Behaviour with Water.—The compound is insoluble in water, but on boiling an oil is produced which dissolves appreciably. The clear hot aqueous solution if rapidly cooled becomes turbid, and after a short time fine needles of the unaltered compound separate, but not without production of some *N*-benzoysalicylamide. Its behaviour with water was studied by diluting an alcoholic solution largely, but insufficiently, to induce separation. The clear solution remained clear for about three hours, after which it became faintly turbid, owing to separation

* If ether is used instead of benzene as a solvent, the whole of the ring-compound is decomposed during the washing with acid.

of the highly insoluble *N*-benzoylsalicylamide, which, however, was not completely precipitated in twenty-four hours. Whether pure water free from carbonic acid would behave like ordinary distilled water has not been tried. Traces of acids (inorganic and organic) enormously accelerate the action of the water, and it was shown roughly that the velocity depends on the concentration of the acid added. If 20 c.c. of a 0.05 per cent. solution are treated with 0.05 c.c. of 10 per cent. hydrochloric acid, the decomposition is complete in about seventy seconds. Accurate velocity measurements have not been made, but the quantitative nature of the conversion was easily shown by decomposing a known weight in dilute alcohol. On acidifying the clear solution with a few drops of hydrochloric acid, after a few seconds a voluminous, microcrystalline precipitate* separated, which was collected and dried at 100°:

0.2230 gave 0.2398 *N*-benzoylsalicylamide.

$C_{14}H_9O_2N$ requires 0.2410 *N*-benzoylsalicylamide.

The purity of the *N*-benzoylsalicylamide was shown by the sharp melting point (206°) before recrystallising.

Behaviour with Acids.—The cyclic compound has only a weakly basic character, and with aqueous acids is decomposed without previously dissolving. It does not yield a picrate in benzene or alcoholic solution. Dry hydrogen chloride in benzene solution precipitates its hydrochloride, which, however, could not be isolated in a pure condition for analysis, owing to the great ease with which it is decomposed by atmospheric moisture.

Behaviour with Alkalis.—With cold aqueous sodium hydroxide and ammonia, the compound is comparatively stable and only very slowly changed to the salt of *N*-benzoylsalicylamide, but sodium hydroxide immediately decomposes it in alcoholic solution. Dry ammonia produces a yellow colour with an alcoholic solution of the compound, and probably an additive compound like that obtained with aniline is formed; this is under investigation.

Behaviour with Phosphorus Pentachloride.—The compound, on treatment with phosphorus pentachloride in presence of chloroform, instantly gives a bright lemon-yellow, crystalline solid,



identical with that obtained by Titherley and Hicks (*loc. cit.*) by the action of phosphorus pentachloride on phenylbenzometoxazone at higher temperatures.

Reduction.—The reduction of 2-phenyl-1:3-benzoxazine-4-one

* The reaction affords a very delicate test for 2-phenyl-1:3-benzoxazine-4-one. On dissolving a minute amount in a drop of alcohol and treating with about 1 c.c. of water and a trace of any dilute acid, a precipitate appears suddenly after a few seconds.

cannot be effected by sodium amalgam, in alkaline solution, or by acid reducing agents, owing to ring rupture. With aluminium amalgam, however, the reduction proceeds rapidly.

A dilute alcoholic solution of the substance was treated with an excess of aluminium amalgam, and water added gradually. When the reduction was complete, the alcoholic solution was filtered and allowed to evaporate. The resulting solid was washed with dilute alkali, dried, and extracted with boiling alcohol. A white, sparingly soluble solid remained behind, which has not yet been identified, and the alcoholic solution deposited needles consisting of impure phenylbenzometoxazone. By carefully recrystallising from alcohol, the latter was obtained pure in fine needles melting at 169° , and was easily identified. The melting point after mixing with a specimen of phenylbenzometoxazone synthesised from salicylamide and benzaldehyde was $168-169^{\circ}$. The yield was about 30 per cent., and a similar reduction performed in an ethereal solution containing 5 per cent. of alcohol gave a yield of 40 per cent.

(b) *Preparation from O-Benzoylsalicylamide*.—A mixture of 3 grams of *O*-benzoylsalicylamide and 30 c.c. of xylene contained in a distilling flask was heated in a bath to 145° , and when the solution became clear a stream of dry hydrogen chloride was passed in for a few minutes. By gradually raising the temperature of the bath to 155° , the xylene was allowed to distil over drop by drop, carrying with it the water formed in the reaction. The hydrogen chloride acted catalytically, and only a relatively small quantity was necessary, but in order to make good that lost by distillation, a few bubbles of the gas were passed into the liquid at intervals of three minutes. The rate of distillation was regulated so that the majority of the xylene had passed over in an hour. About 0.2 gram of water passed over with it, and an oil remained in the flask which partly crystallised on cooling and consisted of a mixture of 2-phenyl-1:3-benzoxazine-4-one and its hydrochloride and unchanged *O*-benzoylsalicylamide, together with a little xylene. When cold it was treated with 20 c.c. of benzene and well shaken with an excess of 3 per cent. sodium hydroxide. A considerable quantity of lemon-yellow solid (the sodium derivative of *N*-benzoylsalicylamide produced by rearrangement of *O*-benzoylsalicylamide) separated, which was mostly removed by repeatedly washing the benzene extract with water. The benzene extract was then dried, filtered, and evaporated at 50° , when large, colourless plates were left, together with an oil which crystallised on cooling. The solid was practically pure 2-phenyl-1:3-benzoxazine-4-one, and weighed 1.8 grams, or 65 per cent. of the theoretical yield. On recrystallising from about 100 c.c. of light petroleum and cooling slowly,

it separated in small, colourless, glistening plates, which melted sharply at 106°, and a mixture with a specimen obtained by the amidine method of synthesis also melted at 106°.

0.2128 g. gave 0.6003 CO₂ and 0.0755 H₂O. C = 76.8; H = 3.9.

0.1812 " 0.5070 CO₂ " 0.0635 H₂O. C = 76.32; H = 3.89.

0.2362 " 13.7 c.c. N₂ (moist) at 23° and 755 mm. N = 6.49.

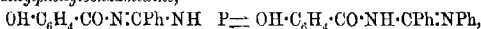
C₁₄H₉O₂N requires C = 75.34; H = 4.03; N = 6.27 per cent.

The properties of the substance agreed in every particular with those of the compound obtained by the amidine method.

In a similar preparation to the above, using toluene instead of xylene as solvent, the compound was also obtained, but the yield was lower (36 per cent. of the theoretical).

(c) *Preparation from N-Benzoylsalicylamide*.—A similar method to the above was employed, using anisole as a solvent at 130°. About two and a-half hours were required for the completion of the change, and a yield of 60 per cent. of 2-phenyl-1:3-benzoxazine-4-one (m. p. 106–107°) was obtained. Ethylene dibromide was also used with success as a solvent, but xylene was unsatisfactory, owing to the small solubility of *N*-benzoylsalicylamide. During the action of the hydrogen chloride, some of the *N*-benzoylsalicylamide is rearranged to *O*-benzoylsalicylamide, and this was isolated in small quantity in one experiment, when xylene was used as solvent, as needles melting with rearrangement at 144°.

Salicylphenylbenzamidine,



was obtained by the action of aniline on 2-phenyl-1:3-benzoxazine-4-one or its hydrochloride by the following methods.

One gram of 2-phenyl-1:3-benzoxazine-4-one and 0.5 gram of aniline were warmed to 50°, and the resulting yellow oil, which did not crystallise on cooling, was dissolved in 50 c.c. of boiling light petroleum and the clear yellow solution allowed to cool slowly. A yellow syrup was deposited, which, after being kept for twelve hours in contact with the mother liquor, changed to a mass of beautiful transparent, yellow needles (1.3 grams), and the mother liquor yielded a further quantity (0.1 gram), the total yield being 93 per cent. of the theoretical.

When instead of light petroleum as a solvent, ether (15 c.c.) was used, the pure compound separated after several hours in clusters of needles (0.9 gram) without any syrup being first deposited, and a further quantity (0.2 gram) was obtained from the mother liquor. The substance was also prepared in the pure state by treating a benzene suspension of 2-phenyl-1:3-benzoxazine-4-one hydrochloride with aniline. The identity of the yellow needles obtained by the

different methods was shown by a comparison of melting point (105—107°) and other properties:

0.2750 gave 19.8 c.c. N_2 (moist) at 17° and 772 mm. $N = 8.50$.

$C_{20}H_{16}O_2N_2$ requires $N = 8.86$ per cent.

Salicylphenylbenzamidine is somewhat sparingly soluble in ether, moderately so in alcohol, and readily soluble in chloroform or benzene. Its solutions give a reddish colour with alcoholic or ethereal ferric chloride. Its solutions on evaporation at the laboratory temperature yield syrups which crystallise completely only after several days, and it is probable that two or more isomeric forms in equilibrium are produced by labile change when the yellow needles are dissolved in any solvent. If heated in a light petroleum solution for any length of time, as in crystallising large quantities, the substance more or less dissociates into aniline and 2-phenyl-1:3-benzoxazine-4-one, which separates to some extent on cooling in colourless needles or tufts alongside the yellow needles of the unchanged substance. Prolonged boiling leads to decomposition of a portion, owing to the action of the aniline (see below) forming diphenylbenzamidine.

Salicylphenylbenzamidine possesses weakly basic and weakly phenolic characters; it is soluble in, but at once decomposed by, hydrochloric acid, yielding *N*-benzoylsalicylamide. In a condition of fine powder it is only very slowly soluble in dilute sodium hydroxide; a yellow solution of the sodium salt results, from which, however, it is apparently impossible to recover the original substance; on acidification with hydrochloric acid, a yellow precipitate is formed, soluble in excess of acid to a nearly clear solution, from which *N*-benzoylsalicylamide is almost instantly precipitated. When salicylphenylbenzamidine is heated at 95°, it dissociates, and eventually melts to a clear yellow liquid with an odour of aniline; if the latter is allowed to evaporate slowly in an open shallow vessel, the yellow colour becomes less conspicuous, and at the end of some hours a colourless liquid results, which finally sets to a mass of colourless plates, consisting of 2-phenyl-1:3-benzoxazine-4-one, the yield of which was almost theoretical. When heated with aniline at 100° for several hours, salicylphenylbenzamidine is partly decomposed into salicylamide and diphenylbenzamidine, the latter obtained in a yield of 35 per cent.

XXIII.—*Iodobenzenemonosulphonic Acids. Part II.*
Esters and Salts of Di- and Tri-iodobenzenesulphonic
Acids.

By MARY BOYLE.

IN the first communication on this subject (Trans., 1909, **95**, 1683) a brief account was given of the preparation of 2:5- and 3:4-di-iodo-benzenesulphonic ethyl esters. It was stated that they were obtained when the sulphonyl chloride was treated either with alcohol in the presence of sodium hydroxide or, when dissolved in ether, with a solution of sodium ethoxide in alcohol, but beyond the further statement that they melted at 113° and 81° respectively, no account of their properties was submitted, and no analytical results were given. Further experiments on ester formation have made clear that neither of the above methods is satisfactory as regards yield and purity of the product unless careful attention is paid to the proportions of interacting substances and to the duration of the action, and the ester melting at 113°, prepared without such attention to detail, proved, on analysis, to be slightly contaminated with the sulphonyl chloride from which it was formed, the pure ester melting about 6° higher. Under the right conditions, however, it has been found possible to esterify all the iodobenzenesulphonic acids discussed in Part I., and to obtain very well-characterised methyl and ethyl derivatives.

Methyl and ethyl benzenesulphonates were prepared by Hübner (*Annalen*, 1884, **223**, 237) by the action of sodium alkyl oxides free from alcohol on solutions of the sulphonyl chlorides in absolute ether, and by Krafft and Roos (*Ber.*, 1892, **25**, 2257) by allowing the chloride to remain for many days at low temperatures in contact with pure methyl and ethyl alcohols respectively; *p*-chloro- and *p*-bromo-benzenesulphonic and certain naphthalenesulphonic methyl and ethyl esters were described by the same experimenters, and the corresponding *p*-iodo-derivative was prepared in 1895 by Kastle and Murrill by the use of sodium ethoxide (*Amer. Chem. J.*, **17**, 290).

In Krafft's experiment with chloride and alcohol alone, the employment of low temperatures seemed imperative, since, as was stated in a later communication (*Ber.*, 1893, **26**, 2823), complete hydrolysis occurred when the two were heated together in sealed tubes, or, in a few cases, when heated for a short time on the water-bath. On the other hand, there is the statement by H. E. Armstrong (*Proc.*, 1891, **7**, 184) that many dibromo-

naphthalenesulphonyl chlorides are readily converted into esters by boiling with excess of alcohol; the 1:4-dibromo-compound being especially remarkable for the ease with which it is esterified, a very small proportion only undergoing hydrolysis; some isomeric sulphonyl chlorides, however, are, according to him, hydrolysed almost completely under exactly the same conditions.

In preparing di- and tri-iodo-benzenesulphonic esters, both methods have been made use of, and it is interesting to note that isomeric acids often behave very differently under similar experimental conditions, the orientation of the molecule appearing to influence to some extent the stability both of the sulphonyl chloride and of the alkylated sulphonic group. The insolubility of most of the sulphonyl chlorides in cold alcohol rendered the success of Krafft's method improbable, and the one experiment which was made proved quite unsuccessful; all of them, however, dissolved in hot alcohol with more or less ease, with gradual esterification.

The tri-iodo- dissolved with much more difficulty than the di-iodo-compounds, and the crystals which separated from the cooled clear solution were much less contaminated with unchanged chloride than was the case when di-iodo-compounds were under investigation. Of the three tri-iodobenzenesulphonyl chlorides investigated, the 3:4:5-derivative dissolved in boiling absolute alcohol with most difficulty and yielded the purest product, the 2:3:5-derivative dissolved with least difficulty, but yielded a product which only became homogeneous after repeated re-solution; the 2:4:5-derivative seemed to lie intermediate between these two.

It seems probable, then, that it is the contiguity of the iodine atom to the sulphonyl chloride group that renders the latter difficult of attack by the alcohol; in every case, however, a hydrolysing action accompanies esterification, the yield of ester under the most favourable conditions never realising more than 60 to 70 per cent.

In the case of the di-iodosulphonyl chlorides, no quantitative experiments have been carried out, but none seem necessary in view of their very decided differences in behaviour towards alcohol.

There is no doubt that the symmetrical 3:5-derivative yields an ester which is practically pure after one recrystallisation, the 2:5- and 3:4-derivatives are attacked with about equal difficulty, and that the 2:4-derivative cannot be made to yield an ester at all by this method, so that here again, with the doubtful exception of the 2:5-derivative, inhibition seems to be a question of the contiguity of the iodine atom and sulphonic group.

The exceptional behaviour of 2:5-di-iodobenzenesulphonyl chloride towards alcohol is in accord with Armstrong's statement with respect to the behaviour of 1:4-dibromonaphthalenesulphonyl

chloride in the same circumstances (*loc. cit.*), and is also at one with the peculiar behaviour of the corresponding 2:5-ester towards alcohol, this ester being more easily hydrolysed by hot alcohol than any of the other ethyl di-derivatives, hydrolysis occurring to the extent of about 39 to 40 per cent. when the two substances are boiled together for five minutes.

The extent to which hydrolysis occurs when iodobenzenesulphonic esters are treated with hot alcohol was investigated in the first instance in order to ascertain the effect of the introduction of a second iodine atom on the stability of the ester. Kastle and Merrill have investigated the behaviour of benzenesulphonic ester and its *p*-chloro-, *p*-bromo-, and *p*-iodo-derivatives towards alcohol both at the ordinary temperature and at 100° (*Amer. Chem. J.*, 1895, 17, 292), and their results show clearly (1) that hydrolysis occurs very slowly at the ordinary temperature, not more than 19 per cent. being attacked in thirty days under the most favourable conditions (one part of ester to 50–100 parts of alcohol), (2) that hydrolysis takes place much more rapidly at 100°, about 9 per cent. undergoing change in five minutes, other conditions being the same, and (3) that the introduction of a halogen atom into the nucleus considerably weakens the stability of the ester, 20 to 21 per cent. now being changed in the same time as before; the three halogens seem to exert practically the same influence.

The introduction of a second and of a third iodine atom into the nucleus would be expected, therefore, still further to diminish the stability of the ester towards alcohol, and experimental results entirely confirm such a view, the average hydrolysis for di-iodo- and tri-iodo-benzenesulphonic esters being, after five minutes at 100°, about 30 to 33 per cent. The experiments, unlike Kastle's, were conducted under atmospheric pressure, equivalent weights of the different esters mixed with the same volume (about fifty times the theoretical amount) of absolute alcohol being heated under reflux in boiling water for five minutes; the cooled mixture was then either diluted with alcohol and titrated with *N*/10-sodium hydroxide, or the unchanged ester was precipitated with water, collected, and the filtrate and washings titrated as before. The latter method is perhaps the better, since the unchanged ester present during titration is slowly hydrolysed by the added sodium hydroxide; on the other hand, this hydrolysing action takes place so slowly that it is comparatively easy to detect the end-point of the acid-neutralisation.

In these experiments it is difficult to compare the tri-iodo- with the di-iodo-esters, and also the tri-iodo-esters among themselves, since two of these, namely, 3:4:5-tri-iodo- and 2:4:5-tri-iodo-

benzenesulphonyl ethyl esters, are so sparingly soluble in alcohol, even after careful powdering, that at the end of the five minutes' heating only a small proportion has passed into solution to be subjected to the hydrolysing action of the alcohol; the 2:3:5-ester, however, is as soluble as the di-iodo-compounds, so that results in the latter cases are strictly comparable. Such results show clearly that the greater the number of iodine atoms in the nucleus, the less the stability of the ethylated sulphonic group, ethyl monoiodobenzenesulphonate, according to Kastle, being hydrolysed to the extent of about 20 per cent. when heated to 100° with alcohol for five minutes, ethyl di-iodobenzenesulphonates, according to the author, undergoing from 25 to 35 per cent. hydrolysis, and ethyl 2:3:5-tri-iodobenzenesulphonate from 45 to 55 per cent.

The results obtained on directly titrating the hydrolysed solution of the ester are always slightly lower than the corresponding ones obtained after precipitation of the unchanged ester, a fact no doubt due to the hydrolysing action of water, which, although very slight and practically negligible at the ordinary temperature for a short period of time, may become of some account after the twelve hours necessary for complete precipitation.

From the experiments on the relative ease of hydrolysis of the four ethyl di-iodobenzenesulphonates, no absolutely definite conclusions can be drawn. All experiments seem to show that the 2:5-ester is the most easily hydrolysed by boiling absolute alcohol, and that the 3:5-ester comes next in order; most experiments place the 2:4-ester next in order of stability, and the 3:4-ester as the most stable of all and least easily affected; some experiments, however, interchange the order of the two latter substances. The following table shows the percentage hydrolysis which occurred in six different experiments:

Ester.	Percentage hydrolysis.					
	(1).	(2).	(3).	(4).	(5).	(6).
2:5-	29	39	—	27	32	—
3:5-	35	36	—	26	—	—
3:4-	24	24	24	24	22	27
2:4-	22	29	29	15	29	30
2:3:5-	57	—	54	59	—	—

The tri-iodo-ester is added for purposes of comparison.

In order to confirm Kastle's statement that the methyl esters are more easily attacked than are the ethyl derivatives by the corresponding alcohols, the action of methyl alcohol on methyl 2:5-di-iodobenzenesulphonate was investigated. Equivalent weights of the ethyl and methyl esters were boiled for five minutes with 10 c.c. of ethyl and methyl alcohol respectively, the unchanged

esters precipitated, and the filtrates titrated with *N*/10-sodium hydroxide.

The following results were obtained:

Ester.	Percentage hydrolysis.
2:5-ethyl ester	39.5
2:5-methyl ester	48

in complete accordance with Kastle's statement.

Since Kraft's method of preparing sulphonic esters had proved unsuccessful, and the method of boiling the sulphonyl chloride with alcohol unsatisfactory, since, also, the method consisting in treating the chloride with warm alcohol in presence of excess of sodium hydroxide resulted, in some cases, in almost complete hydrolysis, and, in all others, in very small yields of ester, the use of sodium alkyloxides was adopted.

In this case, again, poor yields were obtained, until it was recognised that a slight excess of the sodium alkyloxides was sufficient to cause precipitation of sodium iodobenzenesulphonates. By using a standard solution of sodium alkyloxide in absolute alcohol (about 2.5*N*), by adding the slightest excess over the amount necessary to precipitate the chlorine from the sulphonyl chloride, and by keeping the mixture for about half a minute only before addition of water and separation of the ethereal layer, an almost quantitative yield of the ester was obtained. Under these conditions it was found unnecessary to use absolute ether as solvent; methylated ether (dehydrated) dried for some weeks with calcium chloride, and finally with sodium, was found pure enough for practical purposes.

The methyl esters were prepared in exactly the same way, and afforded no difficulty in purification.

Both ethyl and methyl esters crystallise extremely well from alcohol, from ether, and from a mixture of alcohol and ether. In the case of ethyl 2:3:5-tri-iodobenzenesulphonate, two very distinct sets of crystals were obtained from a mixture of alcohol and ether; they melt at the same temperature, and give identical analyses; moreover, one form is transformed into the other on recrystallisation from alcohol; they are evidently the same substance.

Salts of 3:4:5-, 2:4:5-, 2:3:5-tri-iodo-, and of 3:5- and 2:4-di-iodobenzenesulphonic acids, which were not described in Part I, have now been investigated; they are described in the experimental part of this paper.

The following table shows the melting points of the chlorides

and ethyl and methyl esters of di- and tri-iodobenzenesulphonic acids:

Acid.	Chloride.	Ethyl ester.	Methyl ester.
2:5-acid	132°	120.5°	110°
3:5	93	112	100
3:4	82	82	78
2:4	77	57	73
2:3	122.5	110	137
2:4:5-	135	156	160
3:4:5-	145	143	157

EXPERIMENTAL.

2: 4-Di-iodobenzenesulphonic Acid.

The *ethyl* ester was prepared by dissolving the sulphonyl chloride in dry ether and adding the requisite amount of a solution of sodium ethoxide in absolute alcohol; after half a minute, water was added, and the ethereal layer separated and evaporated; the ester separated from alcohol in long needles, melting at 57°:

0.1489 gave 0.1199 CO₂ and 0.0246 H₂O. C=21.99; H=1.83.

C₈H₃O₃I₂S requires C=21.92; H=1.82 per cent.

The *methyl* ester was prepared from the sulphonyl chloride by the use of sodium methoxide in pure methyl alcohol. It crystallises from alcohol in large, plate-like needles, melting at 98°

0.1895 gave 0.1378 CO₂ and 0.0246 H₂O. C=19.84; H=1.44.

C₇H₆O₃I₂S requires C=19.81; H=1.41 per cent.

The *sodium* salt separates from water in white, glistening scales, containing two molecules of water of crystallisation:

0.2019 gave 0.1138 CO₂ and 0.0263 H₂O. C=15.37; H=1.44.

0.9138 lost 0.0702 at 150°. H₂O=7.68.

C₆H₃O₃I₂SNa.2H₂O requires C=15.38; H=1.49;

H₂O=7.68 per cent.

Solubility.—One hundred grams of water dissolve 1.90 grams of anhydrous salt at 13°.

The *potassium* salt crystallises with one molecule of water in sparkling, plate-like needles:

0.2033 gave 0.1151 CO₂ and 0.0199 H₂O. C=15.52; H=1.09.

0.2059 „ 0.0383 K₂SO₄. K=8.35.

0.9375 lost 0.0407 at 145°. H₂O=4.34.

C₆H₃O₃I₂SK.H₂O requires C=15.45; H=1.07; K=8.37;

H₂O=3.86 per cent.

Solubility.—One hundred grams of water dissolve 0.76 gram of the anhydrous salt at 11.5°.

The *ammonium* salt crystallises in glistening, plate-like needles, which are anhydrous.

Solubility.—One hundred grams of water dissolve 2.23 grams at 14°.

3 : 5-Diiodobenzenesulphonic Acid.

The *ethyl* ester crystallises from ether or from a mixture of alcohol and ether in small, white needles, melting at 112°.

0.0591 gave 0.0406 CO₂ and 0.0103 H₂O. C=21.96; H=1.92.

C₈H₅O₃I₂S requires C=21.92; H=1.83 per cent.

The *methyl* ester separates slowly from alcohol in interlacing, plate-like needles, melting at 95°:

0.1159 gave 0.0840 CO₂ and 0.0155 H₂O. C=19.84; H=1.41.

C₇H₅O₃I₂S requires C=19.81; H=1.41 per cent.

The *sodium* salt crystallises in white needles, containing one molecule of water of crystallisation:

0.1286 gave 0.0769 CO₂ and 0.0131 H₂O. C=16.30; H=1.12.

0.4892 lost 0.0195 at 140°. H₂O=3.99.

C₈H₃O₃I₂SNa.H₂O requires C=16.00; H=1.11;

H₂O=4.00 per cent.

Solubility.—One hundred grams of water dissolve 3.56 grams of anhydrous salt at 20°.

The *potassium* salt crystallises in large, white plates; the crystals are anhydrous:

0.1710 gave 0.1014 CO₂ and 0.0112 H₂O. C=16.16; H=0.66.

C₈H₃O₃I₂SK requires C=16.07; H=0.67 per cent.

Solubility.—One hundred grams of water dissolve 0.75 gram of salt at 18.5°.

The *ammonium* salt crystallises in fine, colourless, anhydrous needles.

Solubility.—One hundred grams of water dissolve 1.62 grams of salt at 20°.

The *barium* salt crystallises in colourless needles, containing 1 molecule of water:

0.6225 lost 0.0380 at 145°. H₂O=6.10.

C₁₂H₆O₆I₄S₂Ba.3½H₂O requires H₂O=6.18 per cent.

3 : 4 : 5-Triiodobenzenesulphonic Acid.

Ethyl 3 : 4 : 5-triiodobenzenesulphonate is obtained in a 55 per cent. yield by boiling the sulphonyl chloride with alcohol, in 90 per cent. yield by the use of sodium ethoxide. It separates from alcohol in long, transparent needles, melting at 143°:

0.1865 gave 0.1167 CO₂ and 0.0200 H₂O. C=17.09; H=1.20.

C₈H₃O₃I₃S requires C=17.02; H=1.24 per cent.

Methyl 3: 4: 5-tri-iodobenzenesulphonate crystallises from alcohol in needles, melting at 157° :

0.1461 gave 0.0811 CO_2 and 0.0130 H_2O . $\text{C}=15.15$; $\text{H}=0.98$.

$\text{C}_6\text{H}_2\text{O}_3\text{I}_3\text{S}$ requires $\text{C}=15.27$; $\text{H}=0.90$ per cent.

The *sodium* salt crystallises in small, white, sparkling needles, containing one molecule of water:

0.2642 gave 0.1213 CO_2 and 0.172 H_2O . $\text{C}=12.52$; $\text{H}=0.71$.

1.3331 lost 0.0421 at 150° . $\text{H}_2\text{O}=3.15$.

$\text{C}_6\text{H}_2\text{O}_3\text{I}_3\text{SNa}\cdot\text{H}_2\text{O}$ requires $\text{C}=12.50$; $\text{H}=0.69$;
 $\text{H}_2\text{O}=3.12$ per cent.

Solubility.—One hundred grams of water dissolve 0.86 gram of the anhydrous salt at 15° .

The *potassium* salt separates from water in white, anhydrous needles:

0.2027 gave 0.0944 CO_2 and 0.0073 H_2O . $\text{C}=12.69$; $\text{H}=0.39$.

0.2073 „ 0.0305 K_2SO_4 . $\text{K}=6.59$.

$\text{C}_6\text{H}_2\text{O}_3\text{I}_3\text{SK}$ requires $\text{C}=12.54$; $\text{H}=0.34$; $\text{K}=6.79$ per cent.

Solubility.—One hundred grams of water dissolve 0.128 gram of salt at 16.5° .

The *ammonium* salt crystallises in long, anhydrous needles.

Solubility.—One hundred grams of water dissolve 0.25 gram of salt at 15° .

2: 4: 5-Tri-iodobenzenesulphonic Acid.

Ethyl 2: 4: 5-tri-iodobenzenesulphonate separates from alcohol in glistening crystals, which redissolve with difficulty in alcohol and ether. They melt at $155-156^{\circ}$:

0.1197 gave 0.1117 CO_2 and 0.0188 H_2O . $\text{C}=16.99$; $\text{H}=1.17$.

$\text{C}_8\text{H}_5\text{O}_3\text{I}_3\text{S}$ requires $\text{C}=17.02$; $\text{H}=1.24$ per cent.

Methyl 2: 4: 5-tri-iodobenzenesulphonate separates in small, glistening crystals from a mixture of alcohol and ether. It melts at 166° :

0.1176 gave 0.0656 CO_2 and 0.0089 H_2O . $\text{C}=15.22$; $\text{H}=0.84$.

$\text{C}_7\text{H}_5\text{O}_3\text{I}_3\text{S}$ requires $\text{C}=15.27$; $\text{H}=0.90$ per cent.

The *sodium* salt crystallises in long, fine needles, slightly cream-coloured; they contain $1\frac{1}{2}$ molecules of water:

0.1532 gave 0.0699 CO_2 and 0.0114 H_2O . $\text{C}=12.44$; $\text{H}=0.82$.

0.4245 lost 0.0200 at 135° . $\text{H}_2\text{O}=4.71$.

$\text{C}_6\text{H}_2\text{O}_3\text{I}_3\text{SNa}\cdot 1\frac{1}{2}\text{H}_2\text{O}$ requires $\text{C}=12.31$; $\text{H}=0.85$;
 $\text{H}_2\text{O}=4.61$ per cent.

Solubility.—One hundred grams of water dissolve 0.64 gram of the anhydrous salt at 16.5° .

The *potassium* salt, crystallising in fine, white needles, contains one molecule of water:

0.1458 gave 0.0660 CO_2 and 0.0088 H_2O . $\text{C}=12.34$; $\text{H}=0.68$.

0.4877 lost 0.0163 at 140° . $\text{H}_2\text{O}=3.34$.

0.2111 gave 0.0309 K_2SO_4 . $\text{K}=6.55$.

$\text{C}_6\text{H}_2\text{O}_3\text{I}_3\text{SK}, \text{H}_2\text{O}$ requires $\text{C}=12.16$; $\text{H}=0.67$; $\text{H}_2\text{O}=3.04$;
 $\text{K}=6.58$ per cent.

Solubility.—One hundred grams of water dissolve 0.31 gram of the anhydrous salt at 14° .

The *ammonium* salt crystallises in small, yellow, anhydrous nodules.

Solubility.—One hundred grams of water dissolve 0.82 gram at 11° .

2: 3: 5-Tri-iodobenzenesulphonic Acid.

Ethyl 2: 3: 5-tri-iodobenzenesulphonate separates from a mixture of alcohol and ether in crystals of definite form, somewhat resembling those of copper sulphate; under certain conditions, which have not been definitely fixed, long needles are sometimes obtained; the needles on re-solution in alcohol are changed into crystals of the other form. Both forms melt at 110° , and give identical analytical numbers:

First set (*needles*): 0.1370 gave 0.0849 CO_2 and 0.0167 H_2O .
 $\text{C}=16.91$; $\text{H}=1.35$.

Second set: 0.1867 gave 0.1168 CO_2 and 0.0211 H_2O . $\text{C}=17.06$;
 $\text{H}=1.25$.

$\text{C}_8\text{H}_7\text{O}_3\text{I}_3\text{S}$ requires $\text{C}=17.02$; $\text{H}=1.24$ per cent.

Methyl 2: 3: 5-tri-iodobenzenesulphonate crystallises from a mixture of methyl alcohol and ether in long, transparent needles, melting at 137° :

0.1650 gave 0.0930 CO_2 and 0.0150 H_2O . $\text{C}=15.33$; $\text{H}=1.00$.

$\text{C}_7\text{H}_5\text{O}_3\text{I}_3\text{S}$ requires $\text{C}=15.27$; $\text{H}=0.91$ per cent.

The *sodium* salt probably crystallises with one molecule of water:

0.1531 gave 0.0697 CO_2 and 0.0100 H_2O . $\text{C}=12.41$; $\text{H}=0.71$.

$\text{C}_6\text{H}_2\text{O}_3\text{I}_3\text{SNa}, \text{H}_2\text{O}$ requires $\text{C}=12.50$; $\text{H}=0.69$ per cent.

Solubility.—One hundred grams of water dissolve 0.55 gram of salt at 18° .

The *potassium* salt separates from water in small, glistening crystals containing one molecule of water:

0.2234 gave 0.1021 CO_2 and 0.0155 H_2O . $\text{C}=12.46$; $\text{H}=0.76$.

0.4643 lost 0.0144 at 150° . $\text{H}_2\text{O}=3.10$.

$\text{C}_6\text{H}_2\text{O}_3\text{I}_3\text{SK}, \text{H}_2\text{O}$ requires $\text{C}=12.16$; $\text{H}=0.67$;
 $\text{H}_2\text{O}=3.04$ per cent.

Solubility.—One hundred grams of water dissolve 0.139 gram of the anhydrous salt at 18°.

The ammonium salt is anhydrous. One hundred grams of water contain 0.69 gram at 18°.

Ethyl 2:5-di-iodobenzenesulphonate crystallises from a mixture of ether and alcohol in long, stout needles, melting at 120.5°:

0.1740 gave 0.1411 CO₂ and 0.0296 H₂O. C=22.11; H=1.89.

C₈H₆O₃I₂S requires C=21.92; H=1.83 per cent.

Methyl 2:5-di-iodobenzenesulphonate crystallises from alcohol in woolly needles, melting at 106°:

0.0958 gave 0.0693 CO₂ and 0.0112 H₂O. C=19.72; H=1.29.

C₇H₆O₃I₂S requires C=19.81; H=1.41 per cent.

Ethyl 3:4-di-iodobenzenesulphonate separates from alcohol in needles, melting at 82.5°:

0.1851 gave 0.1483 CO₂ and 0.03 H₂O. C=21.85; H=1.79.

C₈H₆O₃I₂S requires C=21.92; H=1.83 per cent.

Methyl 3:4-di-iodobenzenesulphonate crystallises from methyl alcohol in glistening cubes (?), melting at 93°:

0.1937 gave 0.1414 CO₂ and 0.0262 H₂O. C=19.90; H=1.49.

C₇H₆O₃I₂S requires C=19.81; H=1.41 per cent.

THE ROYAL HOLLOWAY COLLEGE,
ENGLEFIELD GREEN.

XXIV.—A Natural Substantive Dyestuff.

By ARTHUR GEORGE PERKIN.

SOME time ago a small sample of an Egyptian natural dyestuff was received from the authorities of the Imperial Institute, under the name of the "red dura" of the Soudan, the dyeing properties of which proved to be specially interesting in that good shades upon wool could be obtained from it without the aid of a mordant. The material consisted of the leaf sheaths of a grass, smooth externally, possessing a deep reddish-brown tint, and approximately nine inches in length, together with cylindrical fragments of the stem (or pith) of a brighter, although feebler, colour. The following account of this plant was furnished by Mr. C. P. Browne, Inspector of the Blue Nile Province: "I attach a specimen of 'Sikhytan,' the species of durra used for producing a red dye, practically utilised for staining a grass called 'lanzura,' used in the

manufacture of coloured 'bursh' (mats), but occasionally for the leather of 'markuba' (Sudanese shoes). This durra is specially grown for the purpose and not for eating. It occurs in this district, but comes mainly from Rahad, Dinder, and the south." The results of the examination of this product at the Royal Botanic Gardens, Kew, indicated that it was apparently part of the stem, including the leaf sheaths, of the *Andropogon sorghum*, var. *vulgaris*, and this was interesting because this plant, also known as the *Sorghum vulgare*, constitutes the "Great Millet," the grain of which is so important a foodstuff. An elaborate account of the *Sorghum vulgare* is given by Watt ("Dictionary of the Economic Products of India," Vol. 6, Part III, p. 289), and it is worthy of note that in certain cases the grain is described as possessing a brick-red colour, and that at Harihar this is used for preparing a red morocco from goat skin. Again, it is stated in connexion with the *Sorghum saccharatum* that when the pressed canes are allowed to ferment, their colour changes to a red or reddish-brown, and that the dye thus produced can be extracted by means of dilute alkali, and is precipitated from this solution by means of acid in the form of red flakes. The Indian, Persian, Abyssinian, and Egyptian forms would seem to be derived from the *Andropogon sorghum*, var. "durrha" (*ibid.*, p. 278), but the fact that this plant is so extensively cultivated in Egypt as a foodstuff, whereas, according to Browne (*loc. cit.*), the "Sikhytan" is grown entirely on account of its dyeing properties, leaves one to infer that this latter is again a special variety. Unfortunately, but a few ounces of this material were available for examination, and this did not permit of any extended investigation of the colouring matter which is present, but should it be possible to obtain a large quantity of this dyestuff, a more exhaustive study of the subject will then be carried out.

EXPERIMENTAL.

The leaf sheaths and stems (pith) were examined separately, but as experiment showed that the same products were present in both cases, this was evidently not necessary. The material was extracted in a Soxhlet apparatus with boiling acetone until nothing further dissolved, and by evaporating the deep brownish-coloured extract there was obtained from the sheaths 16.27 per cent., and from the pith 14.7 per cent., of a dark brittle resin. On agitating this residue with cold acetone, a small quantity of substance did not pass into solution, and the operation was repeated until the final product was entirely soluble under this treatment. The amorphous substance thus removed, and which, when dry, possessed a slight beetle-green lustre, on incineration yielded some quantity

of ash, and appeared to consist of a calcium salt of the colouring matter. The partly evaporated acetone extract, on treatment with a little boiling benzene, deposited a dull ochre-coloured precipitate almost devoid of tinctorial property, which was removed and the filtrate fractionally evaporated. By this means a gradual separation of the colouring matter was effected, the earlier fractions possessing a deep maroon colour, and those obtained later having a beautiful scarlet tint. The final mother liquid contained, together with some quantity of plant wax, a trace of a yellow, resinous compound.

The crude colouring matter redissolved in a mixture of acetone and benzene was again fractionally crystallised as before, the first and final deposits being rejected, and this appeared to be the only method available in dealing with so small a quantity of the substance. The product consisted of a bright red, almost scarlet, powder, which under the microscope appeared as nodules possessing fine, saw-like edges, and thus possessed an ill-defined crystalline structure. The quantity of colouring matter thus isolated was approximately 3 grams, and of this four distinct preparations, dried at 160°, were analysed:

Found, C=67.27; 67.53; 67.66; 67.40; H=4.40; 4.61; 4.73; 4.33.

$C_{16}H_{12}O_5$ requires C=67.60; H=4.23 per cent.

It is very readily soluble in alcohol, very sparingly so in boiling water, and dissolves in alkaline solutions with a violet-red colour, which rapidly becomes brown owing to oxidation. It is only partly precipitated by excess of alcoholic lead acetate, forming a dull reddish-violet lake soluble in water, but is completely deposited by means of the basic acetate with formation of an insoluble lead salt. With alcoholic ferric chloride it gives a brown coloration, and its solution in both sulphuric and nitric acid is yellow, the latter acid reacting to form a nitro-compound precipitated by water. It does not contain methoxy-groups.

The colouring matter was fused with potassium hydroxide and a little water to 200–220° for twenty minutes, the brownish-coloured mass dissolved in water, and the solution acidified and extracted with ether. The crystalline residue obtained by evaporating the ether, when examined in the usual way, gave phloroglucinol (m. p. 210°) and an acid, melting at 210°, which had all the properties of *p*-hydroxybenzoic acid, and could be admixed with it without alteration of melting point. A second experiment gave also a trace of a compound of lower melting point resembling *p*-hydroxy-acetophenone, but this point requires further corroboration.

Merely a trace of the substance was available for dyeing experiments, but this was sufficient to indicate that the tinctorial

properties of the plant were entirely due to this colouring matter. As was to be expected from its behaviour with lead acetate solution, it does not dye mordanted calico, although as previously indicated, it is a substantive dyestuff towards wool. By the use of a boiling aqueous extract of the plant itself, a dull red shade was obtained with woollen cloth, and this became rather weaker when it was treated with warm dilute soap solution. A very permanent and slightly fuller colour was produced by previously mordanting the wool with chromium or copper, and a similar result could be obtained by an application of the mordant after the dyeing operation. In comparison with the better-known substantive natural dyestuffs, the "red dura" very closely resembles in this behaviour the "insoluble red woods," which contain as the chief colouring matter santalin, and of which sanderswood (*Pterocarpus santalinus*) is a typical example. The shades given by the latter, although of a faintly yellower character, closely resemble those produced by the "red dura," and although the sanderswood possessed somewhat the stronger dyeing power, there was but a trifling distinction to be observed in this respect. Again, it was ascertained that by submitting sanderswood to a similar process to that described above, the colouring matter thus isolated was very similar in appearance and general properties to that obtained from the "red dura." It therefore seems appropriate to term this latter *dura-santalin*.

The formula of santalin, $C_{14}H_{11}O_4(O\cdot CH_3)$ (Cain and May, *J. Soc. Chem. Ind.*, 1909, **28**, 697), does not suggest the existence of a simple chemical relationship between these colouring matters, but it seems likely that they may possess in common a special grouping which will account for their close resemblance.

CLOTHWORKERS' RESEARCH LABORATORY,
THE UNIVERSITY,
LEEDS.

XXV.—*The Effect of Contiguous Unsaturated Groups on Optical Activity. Part IV. Conjugated Systems containing more than Two Unsaturated Groups.*

By SYDNEY ROBERT EDMINSON and THOMAS PERCY HILDITCH.

In the course of work on the effect of two adjacent unsaturated radicles on molecular rotatory power, some of which has already been published in earlier parts of this series, it has been established that a pronounced

increase of optical activity invariably accompanies the conjunction of two such groups. At the same time, it has frequently been noticed that when a third group, possessing marked residual affinity, happens to occur in close proximity to the studied systems, the increase in rotatory power is not always maintained, and, indeed, is sometimes markedly lessened.

This may be instanced from the menthyl esters of piperic and sorbic acids, recently studied by one of us (Trans., 1909, 95, 1570), of which we reproduce here the molecular rotatory powers and corresponding differences from the "normal value" of a menthyl ester (a quantity the approximate estimation of which has already been explained, *loc. cit.*, p. 1571):

	$[M]_D^{20}$	Difference.
$C_6H_5 \cdot CH:CH:CH:CH:CO_2 \cdot C_{10}H_{19}$	-183.3	+28.3
$CH_3 \cdot CH:CH:CH:CH:CO_2 \cdot C_{10}H_{19}$	-221.3	+56.7

The brucine salts of these acids, on the other hand, show a "difference" of +218.8° for the piperate, and +119.5° for the sorbate, under identical polarimetric conditions.

Again, the brucine salts of anthranilic and salicylic acids and their acylated derivatives give evidence of similar irregularities (Trans., 1903, 93, 1388):

	$[M]_D^{20}$	Difference.
Brucine benzoate	-131.1	+118.4
„ anthranilate	-47.8	+201.7
„ acetylanthranilate	+29.8	+279.3
„ benzoylanthranilate	+156.2	+405.7
„ benzoate	-131.1	+118.4
„ salicylate	+75.5	+325.0
„ acetylsalicylate	+86.7	+336.2
„ benzoylsalicylate	± 0.0	+249.5

Since mono-aryl esters of camphoric acid and camphor- β -sulphonic acid can be readily prepared and obtained pure, and since phenolic substances containing as many as five adjacent unsaturated groups are also easily obtainable, we thought it might prove interesting to examine as extended a series as possible of these derivatives. Difficulties appeared, however, in the case of the more complicated phenols used, chiefly owing to the decreasing facility of reaction shown on ascending the series, and to the anticipated fact that the higher esters, although not so strongly coloured as their parent phenols, began to be sufficiently dark yellow to interfere with polarimetric accuracy.

We have endeavoured to arrive at a "normal value" for the molecular rotatory power of acid esters of camphoric acid and of camphor- β -sulphonic esters, in accordance with the usual rule (Tschugaeff, *Ber.*, 1898, 31, 360; Walden, *Ber.*, 1905, 38, 355), by examining the methyl, ethyl, *n*-propyl, and *n*-butyl esters of the two acids. In the case of camphor- β -sulphonic acid, we did not succeed

in obtaining the propyl and butyl compounds in the pure state, and we have therefore used the molecular rotatory power of the ethyl ester as a basis of comparison, since it is well known that the first member of the series is almost always irregular.

We will return to a discussion of the polarimetric results after giving some account of the compounds studied.

EXPERIMENTAL.

The alkyl hydrogen camphorates were prepared according to J. Walker's directions (Trans., 1892, 61, 1088); a quantity of sodium being dissolved in excess of the respective alcohol, the equivalent amount of camphoric anhydride was added, and the mixture boiled for half an hour. The ester was then readily isolated from the sodium salt formed.

Brühl (*Ber.*, 1891, 24, 3409) has observed that ethyl hydrogen camphorate tends to decompose, on being distilled in a vacuum, into the diethyl ester, and camphoric anhydride. We invariably found traces of anhydride in the distillate (under a pressure of 20 mm.) from either the ethyl, *n*-propyl, or *n*-butyl hydrogen esters, and ultimately we purified them by extracting the ethereal solution of the crude product with aqueous sodium hydrogen camphorate. This extract was cooled to 0°, acidified with a slight excess of mineral acid, and extracted again with ether. The dried ethereal extract was filtered, the ether removed by distillation, and the residue heated on the water-bath in a vacuum for two hours. No appreciable decomposition thus took place, and the ethyl hydrogen ester so obtained showed a slightly higher rotation than that hitherto observed.

We should mention that Walker (*loc. cit.*) has proved that in the action of sodium alkyl oxides on camphoric anhydride no *allo*-esters are formed.

Methyl hydrogen camphorate, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_{14}\cdot\text{CO}_2\text{Me}$.—Colourless needles, m. p. 77°:

0.1046 gave 0.2373 CO_2 and 0.0813 H_2O . C = 61.87; H = 8.64.

$\text{C}_{11}\text{H}_{18}\text{O}_4$ requires C = 61.69; H = 8.41 per cent.

Ethyl hydrogen camphorate, $\text{CO}_2\text{H}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}_2\text{Et}$.—A colourless, viscous oil:

0.1004 gave 0.2344 CO_2 and 0.0788 H_2O . C = 63.66; H = 8.72.

$\text{C}_{13}\text{H}_{20}\text{O}_4$ requires C = 63.17; H = 8.77 per cent.

n-Propyl hydrogen camphorate, $\text{CO}_2\text{H}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}_2\cdot\text{C}_3\text{H}_7$.—A colourless, viscous oil:

0.1040 gave 0.2456 CO_2 and 0.0846 H_2O . C = 64.40; H = 9.04.

$\text{C}_{15}\text{H}_{22}\text{O}_4$ requires C = 64.46; H = 9.09 per cent.

VOL. XCVII.

Q

n-Butyl hydrogen camphorate, $\text{CO}_2\text{H}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}_2\cdot\text{C}_4\text{H}_9$.—A colourless oil, much more limpid than the two preceding:

0.1866 gave 0.4525 CO_2 and 0.1516 H_2O . $\text{C} = 66.18$; $\text{H} = 9.03$.
 $\text{C}_{14}\text{H}_{24}\text{O}_4$ requires $\text{C} = 65.63$; $\text{H} = 9.38$ per cent.

The alkylcamphor- β -sulphonates were obtained by heating equivalent amounts of sodium alkoxide and camphor- β -sulphonyl chloride in the respective alcohols for a short time. The product was mixed with ice-water, and, when it had completely solidified, it was collected and recrystallised from aqueous methyl alcohol.

Methyl camphor- β -sulphonate, $\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_3\text{Me}$.—Soft, white needles, melting at 61° :

0.1041 gave 0.2046 CO_2 and 0.0664 H_2O . $\text{C} = 53.60$; $\text{H} = 7.09$.
 0.1630 „ 0.1524 BaSO_4 . $\text{S} = 12.83$.
 $\text{C}_{11}\text{H}_{18}\text{O}_4\text{S}$ requires $\text{C} = 53.67$; $\text{H} = 7.32$; $\text{S} = 13.01$ per cent.

Ethyl camphor- β -sulphonate, $\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_3\text{Et}$.—Wax-like plates, melting at 47° :

0.1064 gave 0.2156 CO_2 and 0.0750 H_2O . $\text{C} = 55.25$; $\text{H} = 7.83$.
 $\text{C}_{12}\text{H}_{20}\text{O}_4\text{S}$ requires $\text{C} = 55.39$; $\text{H} = 7.69$ per cent.

The *n*-propyl and *n*-butyl esters were not obtained solid, either by crystallisation from a number of solvents or on standing in a vacuum desiccator for several weeks, and they were therefore not examined.

The unsaturated compounds studied may be divided into those derived from phenol (*o*-hydroxybenzylidene-acetone and -acetophenone) and from the naphthols (2-aceto- and 2-benzo- α -naphthol) respectively. The latter substances were prepared by heating 10 grams of α -naphthol with 15 grams of zinc chloride and 20 grams of acetic or benzoic acid at 150° for half an hour (Friedländer, *Ber.*, 1895, 28, 1946). Friedländer has characterised 2-aceto- α -naphthol, and shown it to possess the assigned structure, but the similarly formed 2-benzo- α -naphthol does not seem to have been described.

It is obtained in the form of a yellow, amorphous, partly hydrolysed sodium salt on pouring the cold reaction product (see above) into dilute aqueous sodium carbonate; from this salt the phenol itself can be isolated as a yellow, crystalline solid, melting, after recrystallisation from dilute alcohol, at 77° :

0.1039 gave 0.3123 CO_2 and 0.0486 H_2O . $\text{C} = 82.00$; $\text{H} = 5.20$.
 $\text{C}_{17}\text{H}_{12}\text{O}_2$ requires $\text{C} = 82.24$; $\text{H} = 4.84$ per cent.

The benzoyl derivative, prepared by the Schotten-Baumann method, crystallises from light petroleum in pale yellow leaflets, melting at 154° to a dark red liquid:

0.1326 gave 0.3969 CO_2 and 0.0528 H_2O . $\text{C} = 81.68$; $\text{H} = 4.43$.

$\text{C}_{24}\text{H}_{18}\text{O}_2$ requires $\text{C} = 81.83$; $\text{H} = 4.55$ per cent.

2-Benzo- α -naphthol displays a great tendency to form insoluble salts with bases; the pale yellow, amorphous sodium and ammonium salts, and the yellow, crystalline piperidine salt, melting at 138° , are all partly hydrolysed by cold water, but the still less soluble, brownish-yellow barium salt is much more stable:

0.2571 gave 0.0957 BaSO_4 . $\text{Ba} = 21.91$.

$\text{C}_{24}\text{H}_{20}\text{O}_4\text{Ba}$ requires $\text{Ba} = 21.71$ per cent.

The phenolic hydrogen camphorates were obtained according to Schryver's method (Trans., 1899, 75, 661); since, however, it appeared that his directions for preparing the phenolic sodium salts might in some of the present cases give rise to secondary reactions, owing to the presence of metallic sodium, these were prepared by adding the equivalent amount of sodium ethoxide to the phenol in alcohol. After evaporating the alcohol and drying the sodium salt in a vacuum on the water-bath, xylene and the requisite amount of camphoric anhydride were added. With some of the more complex phenols, too prolonged heating appeared to give rise to by-products, a maximum, although frequently not very satisfactory, yield being obtained after heating at 100° for about half-an-hour.

Phenyl hydrogen camphorate, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_5\cdot\text{CO}_2\text{Ph}$.—Slender needles from methyl alcohol, melting at 98° (100° : Schryver):

0.1217 gave 0.3096 CO_2 and 0.0815 H_2O . $\text{C} = 69.38$; $\text{H} = 7.49$.

$\text{C}_{16}\text{H}_{20}\text{O}_4$ requires $\text{C} = 69.56$; $\text{H} = 7.25$ per cent.

α -Acetylvinylphenyl hydrogen camphorate,

$\text{CO}_2\text{H}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CHAc}$.

—Soft, yellow plates from alcohol, decomposing at 111° :

0.1948 gave 0.5006 CO_2 and 0.1237 H_2O . $\text{C} = 70.08$; $\text{H} = 7.05$.

$\text{C}_{20}\text{H}_{24}\text{O}_5$ requires $\text{C} = 69.76$; $\text{H} = 6.98$ per cent.

α -Benzoylvinylphenyl hydrogen camphorate,

$\text{CO}_2\text{H}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CHBz}$,

was not obtained in very good yield; it forms yellow crystals from benzene by precipitation with light petroleum. The compound, which was rather easily hydrolysed, melted at 145° :

0.1104 gave 0.2961 CO_2 and 0.0606 H_2O . $\text{C} = 73.38$; $\text{H} = 6.10$.

$\text{C}_{25}\text{H}_{26}\text{O}_5$ requires $\text{C} = 73.89$; $\text{H} = 6.40$ per cent.

β -Naphthyl hydrogen camphorate, $\text{CO}_2\text{H}\cdot\text{C}_{10}\text{H}_7\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_7$.—Pure white crystals from aqueous alcohol, melting at 125° (121 – 122° : Schryver):

0.1128 gave 0.3073 CO_2 and 0.0740 H_2O . $\text{C} = 74.10$; $\text{H} = 7.29$.

$\text{C}_{20}\text{H}_{22}\text{O}_4$ requires $\text{C} = 73.62$; $\text{H} = 6.75$ per cent.

α-Naphthyl hydrogen camphorate, $\text{CO}_2\text{H}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_7$.—White prisms, which melted somewhat indefinitely at about 170° .

0.1172 gave 0.3163 CO_2 and 0.0734 H_2O . $\text{C} = 73.58$; $\text{H} = 6.96$.

$\text{C}_{20}\text{H}_{22}\text{O}_4$ requires $\text{C} = 73.62$; $\text{H} = 6.75$ per cent.

2-Aceto-α-naphthyl hydrogen camphorate, $\text{CO}_2\text{H}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_6\text{Ac}$.—White needles, melting at 102° :

0.1444 gave 0.3815 CO_2 and 0.0858 H_2O . $\text{C} = 72.05$; $\text{H} = 6.60$.

$\text{C}_{22}\text{H}_{24}\text{O}_5$ requires $\text{C} = 71.74$; $\text{H} = 6.52$ per cent.

2-Benzo-α-naphthyl hydrogen camphorate, $\text{CO}_2\text{H}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_6\text{Bz}$.—A yellow, crystalline powder from benzene, melting and decomposing at 172° :

0.1053 gave 0.2924 CO_2 and 0.0572 H_2O . $\text{C} = 75.30$; $\text{H} = 6.05$.

$\text{C}_{27}\text{H}_{26}\text{O}_5$ requires $\text{C} = 75.34$; $\text{H} = 6.05$ per cent.

The corresponding camphor- β -sulphonates were all prepared by the Schotten-Baumann method, using very dilute aqueous sodium hydroxide and maintaining the reaction solution at such a temperature that the camphor- β -sulphonyl chloride always remained a little above its point of fusion.

Phenyl camphor-β-sulphonate, $\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_3\text{Ph}$, only solidified after standing some time in a vacuum, but thereafter crystallised from light petroleum in long, radiating, colourless needles, melting at 48° :

0.1055 gave 0.2414 CO_2 and 0.0610 H_2O . $\text{C} = 62.38$; $\text{H} = 6.42$.

$\text{C}_{16}\text{H}_{20}\text{O}_4\text{S}$ requires $\text{C} = 62.32$; $\text{H} = 6.49$ per cent.

o-β-Acetylvinylphenyl camphor-β-sulphonate,

$\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_3\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CHAc}$,

was found to be a yellow oil, which would not crystallise, and, as no other means of purification besides crystallisation existed, it could not be utilised.

o-β-Benzoylvinylphenyl camphor-β-sulphonate,

$\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_3\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CHBz}$,

crystallising in yellow needles from benzene, melted at 102° :

0.1000 gave 0.2497 CO_2 and 0.0548 H_2O . $\text{C} = 68.10$; $\text{H} = 6.09$.

$\text{C}_{22}\text{H}_{26}\text{O}_5\text{S}$ requires $\text{C} = 68.48$; $\text{H} = 5.94$ per cent.

β-Naphthyl camphor-β-sulphonate, $\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_3\cdot\text{C}_{10}\text{H}_7$, crystallised in faintly pink prisms from aqueous alcohol, and melted at 100° :

0.0978 gave 0.2396 CO_2 and 0.0549 H_2O . $\text{C} = 66.82$; $\text{H} = 6.24$.

$\text{C}_{20}\text{H}_{22}\text{O}_4\text{S}$ requires $\text{C} = 67.04$; $\text{H} = 6.15$ per cent.

α-Naphthyl camphor-β-sulphonate, $\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_3\cdot\text{C}_{10}\text{H}_7$.—White needles from dilute alcohol, melting at 109° :

0.1097 gave 0.2697 CO_2 and 0.0624 H_2O . $\text{C} = 67.04$; $\text{H} = 6.32$.

$\text{C}_{20}\text{H}_{22}\text{O}_4\text{S}$ requires $\text{C} = 67.04$; $\text{H} = 6.15$ per cent.

2-Aceto-α-naphthyl camphor-β-sulphonate, $\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_3\cdot\text{C}_{10}\text{H}_6\text{Ac}$.—

We will refer, in conclusion, to three other series of this type of compounds, which would seem to exhaust all the available data; the first comprises the camphorates of certain aromatic amines, compared with di-*n*-butylamine camphorate ($[M]_D^{20}$ 38.6 in 2.5 per cent. chloroform solution):

	$[M]_D^{20}$	Difference.
Di- <i>p</i> -toluidine camphorate	+99.4	+60.8
Di- <i>p</i> -aminoacetophenone camphorate	91.2	52.6
Di- <i>p</i> -aminobenzophenone camphorate	73.6	35.0

Next, there are certain condensation products of camphor with aromatic aldehydes:

	$[M]_D^{20}$		$[M]_D^{20}$
Benzylidenecamphor*	+1020	Benzylcamphor*	+343
Cinnamylidenecamphor† ...	788	γ -Phenylpropylcamphor†	178

* Haller, *Compt. rend.*, 1899, 128, 1370.

† Rupe and Frisell, *Ber.*, 1905, 38, 104.

And, finally, certain esters recently examined by Rupe (*Annalen*, 1909, 369, 311):

	$[M]_D^{20}$	Difference.
Menthyl diphenylacetate	-233.4	+75.6
„ α -phenylcinnamate	193.5	+35.7
„ β -phenylcinnamate	137.3	-21.6

Rupe draws the empirical conclusion that a phenyl group in the nearest possible position to the asymmetric system enhances rotatory power, but in others, further removed, depresses it; it appears not a little remarkable that one and the same group should exert a strong influence in two opposing directions, according as it is united with the α - or γ -carbon atoms.

We may summarise these data by pointing out that of the eleven series to which we have referred, four show a steady increase, four show a decrease, and the remaining three manifest indefinite changes in optical activity on increasing beyond two the number of contiguous unsaturated systems. Sufficient facts for a profitable discussion as to whether the indefinite numbers result from conflicting influences other than that due to conjugation, or whether the regular series are simply coincidences, appears still to be lacking.

It will be observed that the difference between the esters of even such nearly related bodies as phenol and *o*-cresol are considerable, and one cause of irregularity may lie in the fact that most of the esters studied above are the earlier members of homologous series, and may thus be abnormal, as has so frequently been noticed in the first members of other series. There is, indeed, little doubt that interesting and more comparable results would follow from a study of active esters of, for example, one of the higher normal aliphatic alcohols, replacing successive methylene groups by a system of multiple,

identical unsaturated groups, but such a series would be very difficult to prepare.

We desire to offer our hearty thanks to Professor Knorr, in whose laboratory this work has been carried out.

UNIVERSITY OF JENA.

XXVI.—*The Constituents of Red Clover Flowers.*

By FREDERICK BELDING POWER and ARTHUR HENRY SALWAY.

THE flowers of the common red clover (*Trifolium pratense*, Linné) have been used to some extent medicinally in recent years on account of their assumed alterative properties, and have even been recommended in the treatment of cancer (*Amer. J. Pharm.*, 1881, 53, 85). So far as known to us, these flowers have never been subjected to a chemical examination, and the only knowledge of their constituents appears to be embodied in a statement that they contain tannin, two resins, fat, and chlorophyll. In this connexion it may incidentally be noted that Perkin and Phipps, in a paper entitled "Notes on some Natural Colouring Matters" (*Trans.*, 1904, 85, 58), have recorded that a cursory examination of the flowers of the white clover (*Trifolium repens*) indicated the presence of quercetin in the form of a glucoside. The same authors furthermore remark that "this colouring matter was recognised by the melting point of its acetyl derivative, and its decomposition products with caustic alkali, and in consequence of these observations a fuller investigation appeared unnecessary."

In view of the above considerations, and the fact that red clover flowers are available in practically unlimited quantities, it appeared desirable that a complete study of their constituents should be undertaken. The present investigation has disclosed the presence of a considerable number of new and interesting substances, and a summary of the results obtained is given at the end of this paper.

EXPERIMENTAL.

The material employed in this investigation was carefully collected for us under the superintendence of Mr. P. E. F. Perrédès, B.Sc., F.L.S., during the month of June, from a field of cultivated red clover (*Trifolium pratense*, Linné) in Kent. The flowers or blossoms were separately gathered, and were therefore, so far as possible, free from the green, herbaceous parts of the plant.

A portion (10 grams) of the dried flowers was tested for an alkaloid, but the reactions obtained were so slight as to indicate the presence of not more than traces of such a substance.

A further portion (25 grams) of the dried flowers was successively extracted in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried in a water-oven, were obtained:

Petroleum (b. p. 35—50°)	extracted	0.50 gram	=	2.0 per cent.
Ether	"	0.50 "	=	2.0 "
Chloroform	"	0.35 "	=	1.4 "
Ethyl Acetate	"	1.50 "	=	6.0 "
Alcohol	"	4.50 "	=	18.0 "

Total 7.35 grams = 29.4 per cent.

For the purpose of a complete examination, 264 kilograms of the flowers were collected. This material, after careful drying, amounted to 58.5 kilograms, or 22.16 per cent. of the original weight. The entire amount of this material was coarsely powdered, and then extracted by continuous percolation with hot alcohol. After the removal of the greater portion of the alcohol, which was conducted at a temperature not exceeding 85°, a dark green, viscous extract was obtained, which amounted to 15.78 kilograms.

Distillation of the Extract with Steam. Separation of an Essential Oil.

A quantity (1.5 kilograms) of the above-mentioned extract was brought into a suitable apparatus with a little water, and steam passed through the mixture for several hours. The distillate, which contained some oily drops, was extracted with ether, the ethereal liquid being washed, dried, and the solvent removed. A small amount (1.5 grams) of an essential oil was thus obtained, which possessed a rather unpleasant odour. On subsequently treating 10 kilograms of the alcoholic extract in the manner above described, a further quantity (10.5 grams) of essential oil was obtained. The yield of oil was thus equivalent to 0.028 per cent. of the dried, or 0.006 per cent. of the fresh clover flowers. This essential oil, when distilled under diminished pressure, passed over between 90° and 160°/20 mm. as a light yellow liquid, which, however, on keeping, ultimately became reddish-brown, and was found to contain furfuraldehyde. It possessed the following constants: $d_{20}^{20}/20^{\circ} = 0.9476$; $\alpha_D^{20} + 4.0'$ in a 1-dm. tube.

Non-volatile Constituents of the Extract.

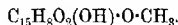
After the removal of the volatile constituents of the extract by distillation with steam, as above described, there remained in the

distillation flask a reddish-brown, aqueous liquid (A) and a quantity of a viscid resin (B), which became solid on cooling. The resin was collected, and thoroughly washed with water, the washings being added to the main portion of the aqueous liquid.

Examination of the Aqueous Liquid (A).

The aqueous liquid was concentrated under diminished pressure, and then repeatedly extracted with large volumes of ether. The ethereal extracts, which were of a light green colour, were united, washed with a little water, dried, and the ether removed, when 10 grams of a dark-coloured, soft solid were obtained. This was found by a preliminary examination to consist of a complex mixture of crystalline compounds, and, in order to obtain a quantity sufficient for their separation and characterisation, 10 kilograms of clover extract were treated as above described, the resulting aqueous liquid being extracted with ether. The yield of ethereal extract from this quantity of material was 64 grams.

Isolation of a New Phenolic Substance, Pratol,



The above-mentioned ethereal extract was digested with a quantity of ether insufficient to dissolve the whole, and the sparingly soluble portion, which amounted to 3 grams, separated by filtration. This product was repeatedly crystallised from alcohol, when a substance was obtained which separated in colourless needles melting at 253° :

0.1265 gave 0.3307 CO_2 and 0.0513 H_2O . $\text{C}=71.3$; $\text{H}=4.5$.

0.1213 „ 0.3161 CO_2 „ 0.0500 H_2O . $\text{C}=71.1$; $\text{H}=4.6$.

$\text{C}_{15}\text{H}_{12}\text{O}_4$ requires $\text{C}=71.6$; $\text{H}=4.5$ per cent.

The above compound, when heated with acetic anhydride, yielded an *acetyl* derivative, which separated from alcohol in feathery needles, melting at 166° . This was analysed, and its molecular weight determined, with the following results:

0.1039 gave 0.2646 CO_2 and 0.0420 H_2O . $\text{C}=69.5$; $\text{H}=4.5$.

0.1069 „ 0.2715 CO_2 „ 0.0436 H_2O . $\text{C}=69.3$; $\text{H}=4.5$.

0.1485, in 33.26 of acetic acid, gave $\Delta t = 0.057^\circ$. $\text{M.W.} = 305$.

$\text{C}_{16}\text{H}_{11}\text{O}_4(\text{CO}\cdot\text{CH}_3)$ requires $\text{C}=69.7$; $\text{H}=4.5$ per cent. $\text{M.W.} = 310$.

The substance $\text{C}_{16}\text{H}_{12}\text{O}_4$ was found to contain one methoxyl group, as determined by Perkin's modification of the Zeisel method:

0.0995 gave 0.0785 AgI . $\text{MeO} = 10.4$.

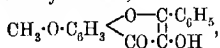
$\text{C}_{15}\text{H}_9\text{O}_3(\text{OMe})$ requires $\text{MeO} = 11.6$ per cent.

No compound of the formula $\text{C}_{16}\text{H}_{12}\text{O}_4$, possessing the same

properties as that above described, appears to have hitherto been recorded. It is therefore proposed to designate the substance from red clover flowers as *pratol*, with reference to its phenolic character and the specific botanical name of the plant.

Pratol, $C_{15}H_8O_3(OH) \cdot O \cdot CH_3$, crystallises in a very characteristic form, since it separates from alcohol in needles, which, under the microscope, are seen to have a talon-like shape with curved edges. It is moderately soluble in hot alcohol, but only sparingly soluble in water, ether, chloroform, or benzene. It dissolves readily in hot aqueous sodium carbonate and sodium hydroxide, yielding pale yellow solutions. When dissolved in acetic anhydride, and a drop of sulphuric acid added, a yellow coloration is produced. With ferric chloride no appreciable change of colour was observed.

Pratol is isomeric with several flavone derivatives, such as the 2-methoxy- and 3-methoxy-flavonol,



prepared by Kostanecki and his co-workers (*Ber.*, 1904, **37**, 775; 1905, **38**, 993). The general behaviour of *pratol* is also very similar to that of the above-mentioned substances, and it therefore seems probable that it represents one of the many hydroxymethoxy-flavones which are theoretically possible.

Acetylpratol, $C_{16}H_{11}O_4(CO \cdot CH_3)$, prepared, as above noted, by heating *pratol* with acetic anhydride, is very soluble in hot alcohol, but only moderately so in chloroform or benzene.

The ethereal liquid from which the sparingly soluble *pratol* had been separated by filtration, as above described, was subsequently shaken with an aqueous solution of ammonium carbonate (*a*) until nothing further was removed by this reagent, then with successive small portions of aqueous sodium carbonate (*b*), and finally with aqueous sodium hydroxide (*c*). These extracts were then separately examined.

Isolation of Salicylic Acid.

The liquids obtained by extraction with ammonium carbonate (*a*) were united, acidified with sulphuric acid, and extracted with ether. This ethereal liquid, on the removal of the solvent, yielded a quantity (20 grams) of a dark green oil. The latter was digested with considerable quantities of hot light petroleum, these liquids being decanted, and the solvent evaporated. In this manner 2 grams of colourless needles were obtained, which, after a few crystallisations from water, melted at 154° and gave an intense violet coloration with ferric chloride:

0.1230 gave 0.2765 CO_2 and 0.0507 H_2O . $\text{C}=61.3$; $\text{H}=4.6$.

$\text{C}_7\text{H}_5\text{O}_3$ requires $\text{C}=60.9$; $\text{H}=4.3$ per cent.

This substance was thus identified as salicylic acid.

The portion of the ammonium carbonate extract which was insoluble in light petroleum was heated for some time with methyl alcohol in the presence of concentrated sulphuric acid. A product was thus obtained which could be further separated into phenolic and non-phenolic methyl esters by shaking its ethereal solution with dilute aqueous sodium hydroxide. The portion insoluble in the alkaline liquid, consisting of the non-phenolic esters, amounted to 10 grams, and was a dark-coloured oil. It was hydrolysed with alcoholic potassium hydroxide, and the regenerated acids distilled under diminished pressure, when fractions were collected at $100-130^\circ$ and $130-230^\circ/20$ mm., whilst a quantity of undistillable resin remained in the flask. These fractions were further examined by neutralising them with aqueous sodium carbonate, and fractionally precipitating the solutions with silver nitrate. A series of silver salts was thus obtained, which, with the exception of the last fraction (III), were more or less brown in colour. After drying in a vacuum over sulphuric acid, they were analysed:

Fraction $100-130^\circ/20$ mm.

0.1760 of salt gave 0.0852 Ag. $\text{Ag}=48.4$.

Fraction $130-230^\circ/20$ mm.

(I) 0.4969 of salt gave 0.1904 Ag. $\text{Ag}=38.4$.

(II) 0.1531 " " 0.0700 Ag. $\text{Ag}=45.7$.

(III) 0.7246 " " 0.4444 Ag. $\text{Ag}=61.3$.

It was evident from these results that the non-phenolic acids consisted of a complex mixture.

Identification of p-Coumaric Acid.

The portion of the above-mentioned methylated product which was soluble in aqueous sodium hydroxide was benzoylated by the Schotten-Baumann method, and then subjected to fractional crystallisation from alcohol. After a quantity of gummy, amorphous matter had been separated, a crystalline substance was deposited, which was ultimately obtained in slender needles, melting at 129° :

0.0783 gave 0.2079 CO_2 and 0.0390 H_2O . $\text{C}=72.4$; $\text{H}=5.5$.

$\text{BzO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Me}$ requires $\text{C}=72.3$; $\text{H}=5.0$ per cent.

This compound is thus seen to agree in composition with the benzoyl derivative of methyl p-coumarate, which hitherto appears not to have been described. A little of it was therefore prepared for the purpose of comparison, when it was found to crystallise in

slender needles, melting at 129° , and to be identical in all respects with the compound obtained from the acid present in red clover flowers. The identity of the latter acid was further confirmed by the hydrolysis of the benzoyl derivative of its methyl ester, when a substance was obtained which crystallised from water in colourless needles, melting at 215° with evolution of carbon dioxide, and otherwise exhibited all the characters of *p*-coumaric acid.

Isolation of a New Yellow Compound, $C_{16}H_{10}O_7$.

The sodium carbonate extracts (*b*), obtained as above described, were separately acidified, and the resulting precipitates collected and examined. The product obtained from the first sodium carbonate extract consisted chiefly of chlorophyll, and nothing crystalline could be isolated from it. The second sodium carbonate extract yielded a yellow powder, which was dissolved in hot alcohol, in which it was freely soluble. This solution, after being kept for some time, deposited a small amount of a colourless, crystalline substance, which, after purification, melted at 253° , and yielded an acetyl derivative melting at 166° . It was found to be identical with the substance $C_{16}H_{12}O_4$, designated as pratol, which has already been described. As the mother liquors, which still contained all of the yellow compound, deposited nothing further on standing, the alcohol was completely removed, and the residue acetylated by means of acetic anhydride. On distilling off the greater part of the latter liquid, a crystalline product separated, which proved to be a mixture of substances. It was fractionally crystallised from alcohol, when a small quantity (1.0 gram) of an acetyl derivative was obtained, which appeared to be homogeneous, and separated in colourless, glistening, prismatic needles, melting at 145 – 147° with evolution of gas:

0.1530 gave 0.3347 CO_2 and 0.0555 H_2O . $C=59.7$; $H=4.0$.

The acetyl content of this compound was determined by heating it for some time with dilute sulphuric acid in the presence of alcohol, the alcohol being then completely removed, and the precipitated yellow substance, which was insoluble in cold water, collected and weighed:

0.1690 gave 0.1108 of yellow substance, or 65.6 per cent.

$C_{16}H_6O_7Ac_4$ requires $C=59.8$; $H=3.7$; $C_{16}H_{10}O_7=65.1$ per cent.
 $C_{16}H_8O_7Ac_2$ " $C=59.5$; $H=4.1$; $C_{16}H_{12}O_7=65.3$ "

It would appear from these results that the yellow compound possesses the formula $C_{16}H_{10}O_7$, and that it contains four hydroxyl groups. The presence of a methoxyl group was also established. The compound, *C. II. O.*, as obtained from its acetyl derivative,

crystallises from boiling dilute alcohol in thin, yellow plates, which melt and decompose at about 280° . It is readily soluble in alcohol or acetic acid, but sparingly so in water, ether, chloroform, or benzene. It dissolves in alkalis with a yellow colour, and its solution in concentrated sulphuric acid exhibits a brilliant green fluorescence. In alcoholic solution it gives with ferric chloride a bluish-black coloration. The amount of this substance available was not sufficient for its further examination.

Isolation of a New Phenolic Substance, Pratenol, $C_{17}H_{10}O_5(OH)_3$.

The final sodium carbonate extract of the above-mentioned etheral liquid yielded, on acidification, a light brown powder. This was dissolved in hot alcohol, and the solution kept for some time, when a small amount of the previously described pratenol, $C_{16}H_{10}O_4$ (m. p. 253°), was deposited. The mother liquors from the latter contained a quantity of a very soluble substance, which could not be obtained directly in a crystalline form. The alcohol was therefore removed, and the residue acetylated, when a product was obtained which, after a few crystallisations from alcohol, yielded a pure, colourless acetyl derivative, melting at 189° :

0.1071 gave 0.2569 CO_2 and 0.0445 H_2O . $C=65.4$; $H=4.6$.

0.1002 „ 0.2410 CO_2 „ 0.0406 H_2O . $C=65.6$; $H=4.5$.

The molecular weight of the acetyl derivative was determined by the ebullioscopic method:

0.3518, in 25.62 of benzene, gave Δt 0.094° . M.W.=390.

$C_{23}H_{18}O_8$ requires $C=65.4$; $H=4.3$ per cent. M.W.=422.

The number of acetyl groups in this compound was ascertained by hydrolysing with aqueous sodium hydroxide, then adding a slight excess of sulphuric acid, and distilling the mixture in a current of steam:

0.2057 gave acetic acid equivalent to 14.45 c.c. $N/10$ -Ba(OH) $_2$.
 $CO \cdot CH_3 = 30.2$.

$C_{17}H_{10}O_5(CO \cdot CH_3)_3$ requires $CO \cdot CH_3 = 30.6$ per cent.

From these results it may be concluded that the substance contained in red clover flowers, from which the above-described triacetyl derivative was prepared, possesses the formula $C_{17}H_{10}O_5$. In order to obtain the parent compound, the acetyl derivative was heated for some time in alcoholic solution with dilute sulphuric acid, and the alcohol subsequently removed by distillation with steam, when a colourless, crystalline substance separated. This was purified by crystallisation from benzene, when it separated in feathery needles, melting at 210° . Although the amount of this substance was insufficient for analysis, it was proved to represent

the original compound by the fact that when again acetylated, it yielded an acetyl derivative melting at 189°.

No compound of the formula $C_{17}H_{12}O_6$, possessing the same properties as that above described, appears to have hitherto been recorded. It is therefore proposed to designate the substance contained in red clover flowers as *pratensol*, with reference to its phenolic character and the specific botanical name of the plant.

Pratensol, $C_{17}H_{12}O_6(OH)_3$, is very readily soluble in alcohol and acetic acid, but only sparingly soluble in water, chloroform, and benzene. It dissolves in alkali carbonates, yielding yellow solutions, whilst its alcoholic solution gives with ferric chloride a greenish-black coloration.

Triacetylpratensol, $C_{17}H_9O_9(CO \cdot CH_3)_3$, crystallises from alcohol, in which it is only moderately soluble, in colourless, slender needles. It is readily soluble in glacial acetic acid, and moderately soluble in benzene. When warmed with dilute aqueous sodium hydroxide, not only are the three acetyl groups removed, but the molecule also undergoes further change, with the formation of a compound which crystallises from dilute alcohol in long, colourless needles, melting at 183–184°. If, on the other hand, the acetyl compound is heated with aqueous sodium carbonate, the product is a yellow, crystalline substance, which melts and decomposes at 160°. It was not possible to ascertain the exact nature of these changes on account of the small amount of substance available, since 37·1 kilograms of dried clover flowers yielded not more than 1·5 grams, or about 0·004 per cent., of pure triacetylpratensol.

Isolation of a New Phenolic Substance, $C_{15}H_8O_3(OH)_3$.

The sodium hydroxide extracts (c) of the previously mentioned ethereal liquid, when acidified, yielded a light green powder, which possessed an odour resembling that of eugenol. An attempt to identify the latter by distilling the product with steam was, however, unsuccessful. The light green powder was subsequently decolorised by treating its hot alcoholic solution with animal charcoal, when, on cooling, colourless clusters of feathery needles separated. After several crystallisations, the substance was obtained pure, and then melted at 225°:

0·0931 gave 0·2133 CO_2 and 0·0310 H_2O . C=62·5; H=3·7.

$C_{15}H_{10}O_6$ requires C=62·9; H=3·5 per cent.

This compound yielded an *acetyl* derivative, which separated from alcohol in thin, silky needles, melting at 209°. The acetyl content of this compound was ascertained by hydrolysing with dilute aqueous sodium hydroxide, then acidifying with sulphuric acid, and distilling the mixture in a current of steam:

0.1750 gave acetic acid equivalent to 12.5 c.c. $N/10\text{-Ba(OH)}_2$.
 $\text{CO}\cdot\text{CH}_3=30.7$.

The molecular weight of the acetyl derivative was also ascertained by the ebullioscopic method:

0.1768, in 26.46 of benzene, gave Δt 0.043° . M.W.=415.

$\text{H}_7\text{O}_6(\text{CO}\cdot\text{CH}_3)_3$ requires $\text{CO}\cdot\text{CH}_3=31.3$ per cent. M.W.=412.

The substance, $\text{C}_{15}\text{H}_{10}\text{O}_6$, is soluble in alkali hydroxides, forming a colourless solution. In alcoholic solution it gives with ferric chloride a dark green coloration. With concentrated sulphuric acid, only a faint yellow colour is produced.

The yield of the substance $\text{C}_{15}\text{H}_{10}\text{O}_6$ was very small, not more than 0.5 gram having been obtained from 37.1 kilograms of dried clover flowers.

Isolation of a New Glucoside, Trifolin, $\text{C}_{22}\text{H}_{22}\text{O}_{11}\cdot\text{H}_2\text{O}$.

The original aqueous liquid (A), which had been extracted with ether, as already described, was kept for a considerable time, when it was observed that a quantity (about 60 grams) of a light brown solid had been deposited. This was collected, and purified by repeated crystallisation from aqueous pyridine, when it separated in minute, slender, pale yellow needles, melting and decomposing at about 260° . The substance contained water of crystallisation, which was lost at 115° , but was again absorbed on exposing the anhydrous substance to the air:

0.3051, on heating at 115° , lost $0.0130\text{ H}_2\text{O}$. $\text{H}_2\text{O}=4.3$.

0.1101 * gave 0.2302 CO_2 and $0.0464\text{ H}_2\text{O}$. $\text{C}=57.0$; $\text{H}=4.7$.

0.1194 * „ 0.2481 CO_2 „ $0.0506\text{ H}_2\text{O}$. $\text{C}=56.7$; $\text{H}=4.7$.

0.1010 * „ 0.2115 CO_2 „ $0.0440\text{ H}_2\text{O}$. $\text{C}=57.1$; $\text{H}=4.8$.

$\text{C}_{22}\text{H}_{22}\text{O}_{11}\cdot\text{H}_2\text{O}$ requires $\text{H}_2\text{O}=3.7$ per cent.

$\text{C}_{22}\text{H}_{22}\text{O}_{11}$ requires $\text{C}=57.1$; $\text{H}=4.8$ per cent.

These results indicated the formula of the above-described substance to be $\text{C}_{22}\text{H}_{22}\text{O}_{11}$, and it proved to be a glucoside. As it is a new compound, it is proposed to designate it *trifolin*, with reference to the generic name of the plant from which it was obtained.

Trifolin, $\text{C}_{22}\text{H}_{22}\text{O}_{11}\cdot\text{H}_2\text{O}$, is insoluble in chloroform, benzene, or in water. It is not readily dissolved by alcohol, but is very soluble in pyridine, and is best crystallised from a mixture of the latter solvent with water. With aqueous sodium carbonate and with alkali hydroxides, it gives intensely yellow solutions. It dissolves in concentrated sulphuric acid, forming at first a yellow solution, but which rapidly develops a brilliant green fluorescence. In alcoholic solution it gives with ferric chloride a dark brown coloration. No crystalline acetyl derivative of trifolin could be prepared.

* Anhydrous substance.

Hydrolysis of Trifolin: Formation of Yellow Colouring Matter, Trifolitin, $C_{16}H_{10}O_6$.

Trifolin was dissolved in alcohol, a little dilute sulphuric acid added, and the mixture heated on the water-bath for an hour. The alcohol was then removed by distillation in a current of steam, when a yellow, crystalline substance separated. This was collected and washed with cold water, the filtrate having been set aside for the subsequent examination of the sugar. Some difficulty was experienced in satisfactorily crystallising the yellow hydrolytic product, for it is extremely soluble in alcohol, and invariably separates from dilute alcohol at the ordinary temperature in an apparently amorphous condition. On the other hand, if the alcohol is removed from the solution at the boiling temperature, the substance then separates from the hot liquid in thin, yellow needles. It is, however, best purified by crystallisation from moist nitrobenzene, when it separates in clusters of slender, yellow needles, which melt and decompose at about 275° . After drying at 130° it was analysed:

0.0786 gave 0.1846 CO_2 and 0.0264 H_2O . $C=64.1$; $H=3.7$.

$C_{16}H_{10}O_6$ requires $C=64.4$; $H=3.4$ per cent.

By heating the yellow hydrolytic product with acetic anhydride an acetyl derivative was obtained. The latter, when crystallised from alcohol, separated in colourless, silky needles, which, when rapidly heated, melted at about 116° , then resolidified, and finally melted at 182° . This behaviour was due to the presence of water of crystallisation, the melting point of the anhydrous substance being 182° :

0.5676, on heating at 105° , lost 0.0231 H_2O . $H_2O=4.1$.

$C_{16}H_6O_6(CO \cdot CH_3)_4 \cdot H_2O$ requires $H_2O=3.7$ per cent.

The anhydrous substance was analysed, and its molecular weight determined, with the following results:

0.1078 gave 0.2426 CO_2 and 0.0401 H_2O . $C=61.4$; $H=4.1$.

0.1056 „ 0.2375 CO_2 „ 0.0391 H_2O . $C=61.3$; $H=4.1$.

0.4012, in 28.14 of phenol, gave $\Delta t = 0.216^{\circ}$. $M.W.=495$.

$C_{16}H_6O_6(CO \cdot CH_3)_4$ requires $C=61.8$; $H=3.9$ per cent. $M.W.=466$.

In order to ascertain the number of acetyl groups in the above compound, it was dissolved in alcohol, dilute sulphuric acid added, and the mixture heated for several hours on the water-bath. The alcohol was then completely removed by distillation in a current of steam, and, after cooling, the precipitated yellow substance was collected and weighed, it having been found that the amount dissolved by the water was negligible:

0.1811 gave 0.1160 of colouring matter, or 64.1 per cent.

0.2922 " 0.1876 " 64.2 "

$C_{16}H_{10}O_6(CO \cdot CH_3)_4$ requires $C_{16}H_{10}O_6 = 63.9$ per cent.

The yellow colouring matter, as obtained from the above-described acetyl derivative, was crystallised from dilute alcohol, dried at 120° , and again analysed:

0.0855 gave 0.2000 CO_2 and 0.0276 H_2O . $C = 63.8$; $H = 3.6$.

$C_{16}H_{10}O_6$ requires $C = 64.4$; $H = 3.4$ per cent.

It is evident from the above results that the yellow colouring matter obtained by the hydrolysis of the glucoside trifolin possesses the formula $C_{16}H_{10}O_6$, and that it contains four hydroxyl groups. As no compound of this formula, having the same properties, has hitherto been recorded, it is proposed to designate it *trifolit*.

Trifolit, $C_{16}H_{10}O_6$, is readily soluble in alcohol and glacial acetic acid, but only very sparingly soluble in benzene, chloroform, or ether. It dissolves in alkalis with an intense yellow colour, and dyes mordanted cotton wool a bright yellow. When dissolved in concentrated sulphuric acid, it gives a yellow solution, followed by a brilliant green fluorescence. It is precipitated from its alcoholic solution by basic lead acetate as an orange-yellow lead salt. In alcoholic solution it gives with ferric chloride a dark green coloration. *Trifolit* is not altered when heated for several hours with 30 per cent. aqueous potassium hydroxide, and it contains no methoxyl group. It is evident from its empirical formula, $C_{16}H_{10}O_6$, that it cannot belong to the flavone group of natural colouring matters, and it differs, moreover, from the flavone compounds by the fact that it forms no salt with sulphuric acid (Trans., 1896, 80, 206), whilst it is only with difficulty that a potassium salt is deposited from its concentrated alcoholic solution on the addition of potassium acetate. On the other hand, the composition and general properties of *trifolit* would agree with those of a tetrahydroxy-derivative of phenyl-naphthaquinone, but the amount of material available was not sufficient to enable us definitely to ascertain the group of naturally occurring dyes to which it belongs.

The aqueous liquid obtained in the course of hydrolysis of the glucoside trifolin was treated with barium carbonate for the removal of the sulphuric acid, and evaporated to the consistency of a syrup. This liquid readily reduced Fehling's solution, and yielded a crystalline osazone which, in the crude condition, melted and decomposed at 180° . When crystallised from aqueous pyridine, it separated in needles, which melted and decomposed at 194° :

0.1258 gave 0.2902 CO_2 and 0.0738 H_2O . $C = 62.9$; $H = 6.5$.

$C_{15}H_{22}O_3N_4$ requires $C = 63.2$; $H = 6.4$ per cent.

The above result indicated that the sugar formed by the VOL. XXVII.

hydrolysis of trifolin has the formula $C_{22}H_{32}O_{11}$, and it appeared to be rhamnose, the osazone of which, however, is stated to melt at 180° . For the purpose of comparison, an osazone was prepared from a commercial specimen of rhamnose. This, when crystallised from aqueous pyridine, was found to melt and decompose at 188° , and appeared to be identical with that above described. Trifolin is therefore converted by hydrolysis into trifolitin and rhamnose. A known weight of the glucoside was subsequently hydrolysed by dilute sulphuric acid in aqueous alcohol, the alcohol then removed by passing steam through the mixture, and, after cooling, the precipitated trifolitin was collected, washed with cold water, dried at 120° , and weighed:

0.2056 gave 0.1318 of hydrolytic product, or 64.1 per cent.

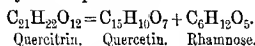
0.2885 " 0.1859 " " 64.4 "

$C_{22}H_{32}O_{11}$ requires $C_{16}H_{20}O_6 = 64.5$ per cent.

The hydrolysis of trifolin therefore takes place according to the following equation:



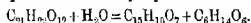
This equation would appear to indicate that the formation of trifolitin and rhamnose from trifolin is unaccompanied by the absorption of water, and would thus be analogous to that representing the hydrolysis of quercitrin*:



The explanation of this apparent anomaly may be, either that these glucosides tenaciously retain a molecule of water, or that the respective phenolic hydrolytic products suffer dehydration immediately after their formation.

The dark-coloured aqueous liquid from which the above-described glucoside, trifolin, had separated was next shaken repeatedly with hot amyl alcohol. The amyl alcohol extracts were united, washed with a little water, and then concentrated under diminished pressure, when, on cooling, a yellow, gelatinous substance was deposited. This was removed by filtration, and the filtrate again concentrated, when a further quantity of a yellow substance was obtained. To the final amyl-alcoholic filtrate, light petroleum was added, which

* The hydrolysis of quercitrin is usually represented as follows:



This equation, however, is evidently incorrect, inasmuch as it is now known that rhamnose possesses the formula $C_6H_{12}O_5$, but crystallises with one molecule of water (compare A. G. Perkin, *J. Soc. Chem. Ind.*, 1903, 22, 602, and Brauns, *Arch. Pharm.*, 1904, 242, 561).

precipitated the remainder of the yellow substance as an amorphous powder. The three fractions thus obtained were separately examined.

Fraction I.—This product consisted of a yellow, highly hygroscopic substance. It was dissolved in hot alcohol, and the solution kept for some time, when a gelatinous, brown mass separated. The latter was twice subjected to the preceding treatment with alcohol, when a crystalline substance was obtained, which was finally purified by crystallisation from dilute alcohol. It then formed colourless, glistening leaflets, melting at 214° . The amount of pure substance isolated was 0.5 gram:

0.0989 gave 0.2199 CO_2 and 0.0440 H_2O . $\text{C}=60.6$; $\text{H}=4.9$.

0.1154 „ 0.2559 CO_2 „ 0.0496 H_2O . $\text{C}=60.5$; $\text{H}=4.8$.

$\text{C}_{14}\text{H}_{12}\text{O}_6$ requires $\text{C}=60.9$; $\text{H}=4.3$ per cent.*

This substance would thus appear to possess the formula $\text{C}_{14}\text{H}_{12}\text{O}_6$, and, as it differs in its properties from any substance of this formula which has hitherto been recorded, it may be regarded as a new compound.

The compound, $\text{C}_{14}\text{H}_{12}\text{O}_6$, is insoluble in water, chloroform, or benzene, but readily soluble in hot alcohol. It is insoluble in aqueous sodium carbonate, but readily dissolves in alkali hydroxides without change of colour. It gives no coloration with concentrated sulphuric acid, and is not changed by heating with dilute sulphuric acid. Its alcoholic solution yields with ferric chloride a light green coloration.

Isolation of a Second Glucoside of Trifolitin, isoTrifolitin, $\text{C}_{22}\text{H}_{22}\text{O}_{11}$.

Fraction II.—This product, consisting of a light yellow powder, was fractionally crystallised from alcohol. The more soluble portion contained a substance which separated from very dilute alcohol in pale yellow needles, melting and decomposing at about 250° with the formation of a deep red liquid. It was dried at 115° :

0.1100 gave 0.2282 CO_2 and 0.0451 H_2O . $\text{C}=56.6$; $\text{H}=4.6$.

$\text{C}_{22}\text{H}_{22}\text{O}_{11}$ requires $\text{C}=57.1$; $\text{H}=4.8$ per cent.

The glucosidic character of this substance was proved by heating with dilute sulphuric acid in aqueous alcohol. On removing the alcohol, a yellow colouring matter separated from the hot solution in thin needles, which melted and decomposed at 275° . This hydrolytic product yielded an acetyl derivative, which was found to be identical with that prepared from the previously described trifolitin, $\text{C}_{16}\text{H}_{16}\text{O}_6$. The aqueous liquid obtained in the course of the above hydrolysis readily reduced Fehling's solution, but the amount of glucoside available (0.5 gram) did not permit of preparing an osazone from the sugar.

Although the above-described glucoside yields the same yellow hydrolytic product, and possesses apparently the same empirical formula as the glucoside trifolin, the two compounds are evidently not identical. Thus trifolin (m. p. 260°) separates from dilute alcohol in small, globular aggregates of fine needles, whilst the glucoside, melting at 250° , is much more soluble, and crystallises in clusters of comparatively large needles. It is therefore proposed to designate the second glucoside of trifolitin as *isotrifolin*.

The general behaviour of *isotrifolin*, as might be expected, is very similar to that of trifolin. It dissolves in alkalis with the formation of a deep yellow solution. With concentrated sulphuric acid, a yellow coloration is produced, together with a green fluorescence, and in alcoholic solution it gives with ferric chloride a deep brown colour.

Isolation of a Glucoside of Quercetin.

The sparingly soluble portion of the above-described fraction II was finally purified by crystallisation from water, when it separated in pale yellow, prismatic needles, melting and decomposing at 235° : 0.1484, on heating at 110° , lost 0.0161 H_2O . $H_2O = 10.8$. 0.1117, dried at 110° , gave 0.2184 CO_2 and 0.0475 H_2O . $C = 53.3$; $H = 4.7$.

The substance dissolved readily in hot water, giving a yellow solution, the colour of which was greatly intensified by the addition of alkalis. With concentrated sulphuric acid, a green fluorescence was produced. Its aqueous solution gave with ferric chloride a dark green coloration.

On heating the substance for a short time in aqueous solution with dilute sulphuric acid, a crystalline, yellow compound separated, and the filtrate from the latter readily reduced Fehling's solution. It was thus evident that the substance was a glucoside. The yellow hydrolytic product melted and decomposed at 305° , and, by means of its acetyl derivative (m. p. 195°), was identified as quercetin. The amount of this glucoside obtained from 37.1 kilograms of dried red clover flowers was only about 0.5 gram, and it was therefore not possible more definitely to characterise it.

Fraction III.—This was a yellow, amorphous solid, which was freely soluble in alcohol, giving a dark-coloured solution. The attempts to obtain something crystalline from this solution were unsuccessful, and as a preliminary test indicated the presence of glucosidic substances, the whole of the fraction, together with the mother liquors from fractions I and II, was hydrolysed by heating for some time with dilute sulphuric acid in aqueous alcohol. After removing the alcohol, a quantity of a dark-coloured solid separated.

which was collected and washed with water. This product was found to be a highly complex mixture, which, however, by digestion with ether, could be separated into readily and sparingly soluble portions. The ethereal solution of the readily soluble portion was extracted with alkalis, when it yielded traces of salicylic acid, a small amount of pratol, $C_{16}H_{12}O_4$, and a yellow compound melting at 305° , which, by means of its acetyl derivative (m. p. 194°), was identified as quercetin.

Isolation of isoRhamnetin, $C_{16}H_{12}O_7$.

The portion of the above-mentioned hydrolytic product which was sparingly soluble in ether was treated with aqueous sodium carbonate, when it was found to be only partly soluble in the alkaline liquid. From the insoluble portion a small amount of the previously described compound, $C_{14}H_{10}O_6$ (m. p. 214°), was obtained, whilst the portion soluble in the alkali carbonate consisted chiefly of a yellow colouring matter, which was observed to differ from any of the substances already isolated from the clover flowers. This substance was sparingly soluble in acetic acid and alcohol, and was purified by conversion into its acetyl derivative, the latter being then fractionally crystallised from alcohol until constant in melting point. It then separated in thin, hair-like needles, melting at $198-200^\circ$. After being dried at 120° :

0.0927 gave 0.2017 CO_2 and 0.0354 H_2O . $C=59.3$; $H=4.2$.

$C_{16}H_8O_7(CO \cdot CH_3)_4$ requires $C=59.5$; $H=4.1$ per cent.

The number of acetyl groups in this derivative was determined by hydrolysis with dilute sulphuric acid, the hydrolytic product being then collected and weighed:

0.1120 gave 0.0722 of colouring matter, or 64.5 per cent.

0.1126 „ 0.0734 „ „ 65.2 „

$C_{16}H_8O_7(CO \cdot CH_3)_4$ requires $C_{16}H_{12}O_7=65.3$ per cent.

The hydrolytic product, which melted and decomposed at about 295° , was a deep yellow substance, only sparingly soluble in alcohol or acetic acid, and insoluble in chloroform or benzene. It dissolved in alkalis, with the production of a deep yellow colour, and its solution in sulphuric acid possessed a green fluorescence. It was found to contain one methoxyl group, as determined by Perkin's modification of the Zeisel method:

0.0941 of acetyl compound gave 0.0379 AgI. $MeO=5.3$.

$C_{15}H_8O_6(OCH_3)(CO \cdot CH_3)_4$ requires $MeO=6.4$ per cent.

From these analytical data it may be concluded that the yellow substance has the empirical formula $C_{16}H_{12}O_7$, and that it contains four hydroxyl groups and one methoxyl group. The composition

and characters of this substance are thus in agreement with those of isorhamnetin, a colouring matter which was first isolated by A. G. Perkin (Trans., 1896, 69, 1658) from the petals of the yellow wallflower (*Cheiranthus Cheiri*). The last-mentioned author had, however, recorded the melting point of tetra-acetylisorhamnetin as 195—196°.

In order to further confirm the identity of the substance contained in red clover flowers with isorhamnetin, the product resulting from the methoxyl determination was examined. This separated from the acid solution, on cooling, in yellow, silky needles, which did not melt, but partially volatilised, at a temperature below 300°. It gave an acetyl derivative melting at 190—192°, and possessed the general characters of quercetin, thus affording conclusive evidence that the respective substance in red clover flowers was a monomethyl derivative of quercetin and identical with isorhamnetin.

The aqueous liquid which had been extracted with hot amyl alcohol, as above described, was dark brown in colour, and gave an abundant yellow precipitate on the addition of basic lead acetate. This precipitate was examined in the usual way, but, with the exception of a small amount of yellow colouring matter, nothing definite could be isolated from it. The filtrate from the basic lead acetate precipitate, after removal of the excess of lead, was of a bright yellow colour, and readily reduced Fehling's solution. It contained a large quantity of sugar, which yielded *d*-phenylglucosazone, melting at 205°. The liquid was concentrated under diminished pressure to the consistency of a syrup, and kept for a considerable time, but nothing crystalline separated from it.

The Resins (B).

The resinous material obtained from 1.5 kilograms of the original alcoholic extract of red clover flowers was a dark green, soft solid, and amounted to 314 grams. It was dissolved in alcohol, the solution mixed with purified sawdust, and the thoroughly dried mixture then successively extracted in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100°, were obtained:

Petroleum (b. p. 30—45°) extracted	190.0 grams = 60.5 per cent.
Ether	19.0 " = 6.1 "
Chloroform	6.7 " = 2.1 "
Ethyl Acetate	10.3 " = 3.3 "
Alcohol	48.0 " = 13.7 "
Total	269.0 grams = 85.7 per cent.

Petroleum Extract of the Resin.

This extract consisted of a dark green, semi-solid fat. It was hydrolysed by heating for a short time with an alcoholic solution of potassium hydroxide, after which the alcohol was removed, water added, and the alkaline mixture repeatedly extracted with ether. The ethereal extracts were united, washed, dried, and the solvent removed, when a quantity (46.5 grams) of a brownish-yellow solid was obtained.

Isolation of Myricyl Alcohol, $C_{31}H_{63}\cdot OH$.

The above-mentioned, brownish-yellow, unsaponifiable material was agitated with cold alcohol, and thus separated into a soluble and an insoluble portion. The latter consisted of a colourless, wax-like solid, melting somewhat indefinitely at $70-74^{\circ}$. It appeared to consist of a mixture of several substances, and was therefore subjected to prolonged fractional crystallisation from a mixture of ethyl acetate and alcohol. In this manner the least soluble constituent was ultimately obtained pure, and then melted at 85° . It crystallised from ethyl acetate in small, colourless needles, whilst from alcohol it separated in glistening leaflets:

0.1250 gave 0.3776 CO_2 and 0.1597 H_2O . $C=82.4$; $H=14.2$.

$C_{31}H_{64}$ requires $C=82.3$; $H=14.2$ per cent.

The analysis and properties of this substance establish its identity as myricyl alcohol.

Isolation of Heptacosane, $C_{27}H_{56}$, Hentriacontane, $C_{31}H_{64}$, and Sitosterol, $C_{27}H_{46}O$.

The more soluble substances obtained in the course of the above fractionation could not be further separated by crystallisation. A preliminary examination having indicated that they consisted chiefly of hydrocarbons, with presumably a little myricyl alcohol, the mixture was heated at 130° for an hour with an equal weight of phthalic anhydride, in order to convert the myricyl alcohol into its acid phthalic ester, and thus effect its removal. The product was subsequently digested with a mixture of ether and chloroform, the solution filtered, and shaken with aqueous sodium carbonate. An insoluble compound thus separated, which was collected, and found to consist of myricyl sodium phthalate. The ether-chloroform solution was then evaporated, and the residue heated with aqueous sodium hydroxide in order to remove unchanged phthalic anhydride. The portion insoluble in the alkali was afterwards dissolved in chloroform, the solution being washed, dried, and the solvent

removed. A wax-like solid was thus obtained, which was subjected to fractional crystallisation from ethyl acetate. The most sparingly soluble fraction, which separated in pearly leaflets, melted at 65° , and this melting point was not changed by further crystallisation:

0.1001 gave 0.3121 CO_2 and 0.1324 H_2O . $\text{C}=85.0$; $\text{H}=14.7$.

$\text{C}_{31}\text{H}_{64}$ requires $\text{C}=85.3$; $\text{H}=14.7$ per cent.

This substance was evidently hentriacontane (m. p. 68°), the somewhat low melting point being probably due to the presence of a small amount of the following hydrocarbon.

From the more readily soluble fractions, a substance was isolated which separated in pearly leaflets, melting at $58-59^{\circ}$:

0.0944 gave 0.2943 CO_2 and 0.1229 H_2O . $\text{C}=85.0$; $\text{H}=14.5$.

$\text{C}_{27}\text{H}_{56}$ requires $\text{C}=85.3$; $\text{H}=14.7$ per cent.

This substance was thus identified as heptacosane.

The portion of the unsaponifiable material which was soluble in cold alcohol amounted to 30.2 grams. It was twice distilled under diminished pressure, and the following five fractions collected: 200— 210° ; 210— 220° ; 220— 290° ; 290— 300° ; and above $300^{\circ}/2$ mm.

Fraction 200— $210^{\circ}/20$ mm.—This was a pale yellow liquid, and contained a considerable quantity of an unsaturated substance:

0.1083 gave 0.3256 CO_2 and 0.1289 H_2O . $\text{C}=82.0$; $\text{H}=13.2$.

0.1234 absorbed 0.1008 iodine. Iodine value = 81.7.

Fraction 210— $220^{\circ}/20$ mm.—This was a brownish-yellow liquid and, like the preceding fraction, was unsaturated:

0.1064 gave 0.3141 CO_2 and 0.1288 H_2O . $\text{C}=80.5$; $\text{H}=13.5$.

0.0990 absorbed 0.0832 iodine. Iodine value = 84.0.

Both the above fractions were evidently mixtures, and nothing of a definite nature could be obtained from them.

Fractions 220— 290° ; 290— 300° ; and above $300^{\circ}/20$ mm.—The fractions solidified on cooling, and were found to consist chief of a phytosterol, with a small quantity of the previously mentioned hydrocarbons. After repeated crystallisation, a substance was isolated which separated from a mixture of ethyl acetate and alcohol in colourless, glistening leaflets, melting at $135-136^{\circ}$:

0.3194, on heating at 110° , lost 0.0160 H_2O . $\text{H}_2\text{O}=5.0$.

$\text{C}_{27}\text{H}_{46}\text{O}, \text{H}_2\text{O}$ requires $\text{H}_2\text{O}=4.5$ per cent.

0.0963, dried at 110° , gave 0.2959 CO_2 and 0.1033 H_2

$\text{C}=83.8$; $\text{H}=11.9$.

$\text{C}_{27}\text{H}_{46}\text{O}$ requires $\text{C}=83.9$; $\text{H}=11.9$ per cent.

0.2244 of anhydrous substance, made up to 25 c.c. with chloroform, gave $\alpha_D -1.0^{\circ}37'$ in a 2 dcm. tube, whence $[\alpha]_D -34.4^{\circ}$.

The above-described substance was evidently a phytosterol, and it gave the four reactions of this class of compounds. It yielded an acetyl derivative, melting at 126° , and therefore is identical with sitosterol (*Monatsh.*, 1897, 18, 551).

Isolation of a New Dihydric Alcohol, Trifolianol, $C_{21}H_{34}O_2(OH)_2$

The aqueous alkaline solution of potassium salts resulting from the hydrolysis of the petroleum extract of the resin, having been shaken with ether to remove unsaponifiable material, as already described, was acidified with dilute sulphuric acid, when a dark coloured semi-solid precipitate of fatty acids was produced. On extracting the mixture with ether, however, it was observed that a portion of the precipitate was very sparingly soluble in that liquid. The sparingly soluble material was therefore collected, when it formed a pale green solid, amounting to 3 grams. It was purified by crystallisation from pyridine containing a little alcohol, from which it was deposited in minute, colourless needles, melting and decomposing at 295° . After being dried at 110° :

0.1049 gave 0.2746 CO_2 and 0.0982 H_2O . $C = 71.4$; $H = 10.4$.

$C_{21}H_{36}O_4$ requires $C = 71.6$; $H = 10.2$ per cent.

This compound yielded an acetyl derivative, which separated from alcohol in flat, colourless needles, melting at $165-166^{\circ}$. Analysis and the determination of its optical rotatory power gave the following results:

0.0968 gave 0.2442 CO_2 and 0.0799 H_2O . $C = 68.8$; $H = 9.2$.

$C_{21}H_{34}O_4(CO \cdot CH_3)_2$ requires $C = 68.8$; $H = 9.2$ per cent.

0.2435, made up to 25 c.c. with chloroform, gave $\alpha_D - 0^{\circ}30'$ in a 2-dcm. tube, whence $[\alpha]_D - 25.7^{\circ}$.

From the above results it was evident that the compound melting at 295° is a dihydric alcohol, having the empirical formula $C_{21}H_{34}O_4$. As it is a new substance, it is proposed to designate it *trifolianol*, with reference to the generic name of the plant from which it was obtained.

Trifolianol, $C_{21}H_{34}O_2(OH)_2$, is practically insoluble in water, and very sparingly soluble in alcohol, ether, and chloroform, but readily soluble in dilute pyridine, from which it crystallises in minute needles. When dissolved in chloroform with a little acetic anhydride, and a drop of concentrated sulphuric acid subsequently added, it gives a transient pink coloration, changing to blue, and finally to green. The properties of trifolianol are similar to those of two other dihydric alcohols which have recently been isolated in these laboratories, namely, ipuranol, $C_{28}H_{38}O_2(OH)_2$ (*Amer. J. Pharm.*, 1908, 80, 264, 576; *Trans.*, 1908, 93, 907; 1909, 95, 249),

and citrullol, $C_{22}H_{36}O_2(OH)_2$ (this vol., p. 102). These alcohols therefore appear to be members of a homologous series, which is represented by the general formula, $C_nH_{2n-6}O_4$.

Examination of the Fatty Acids.

The ethereal solution, from which the above-described trifolanol had been removed by filtration, was washed, dried, and the solvent removed. The mixture of fatty acids thus obtained contained a considerable quantity of resinous material, which was insoluble in light petroleum, and was therefore removed by digesting the mixture with the latter solvent, and filtering. This resin was a dark green solid, amounting to 10 grams, but no definite crystalline compound could be isolated from it. The petroleum solution, on evaporation, yielded a dark-coloured mixture of fatty acids, which was distilled under diminished pressure. The pale yellow distillate, amounting to 60 grams, became partly solid on cooling. It was dissolved in alcohol, when a substance separated which, after several crystallisations from alcohol, melted at $60-61^\circ$:

0.1182 gave 0.3236 CO_2 and 0.1341 H_2O . $C=74.7$; $H=12.6$.

0.1280 required for neutralisation 5.02 c.c. $N/10$ -KOH.

Neutralisation value = 220.

$C_{16}H_{32}O_2$ requires $C=75.0$; $H=12.5$ per cent.

Neutralisation value = 219.1.

This substance was thus identified as palmitic acid.

In order to ascertain the nature of the remaining constituents of the mixed fatty acids, the mother liquors from the above crystallisations were united, and, while hot, fractionally precipitated with a concentrated aqueous solution of barium acetate. The final precipitate was oily, and, as it consisted for the most part of the barium salts of unsaturated acids, it was separately examined as described below. From the other fractions of barium salt the fatty acids were regenerated, and, after one crystallisation from acetic acid, were titrated with a decinormal solution of potassium hydroxide. The neutralisation values of the several fractions were 199.0; 210.0; 213.0; 213.5; 214.8; and 216.9, whilst their melting points were $53-55^\circ$; $53-56^\circ$; $53-56^\circ$; $53-56^\circ$; $54-56^\circ$; and $56-59^\circ$ respectively. These results indicated that the saturated acids consisted chiefly of a mixture of palmitic and stearic acids, the respective neutralisation values of which are 219.1 and 197.7.

The acids obtained from the above-mentioned oily barium salt were converted into their lead salts, and the latter treated with ether. From the portion of lead salt which was undissolved by the ether, a further small amount of palmitic acid was obtained. The acids regenerated from the soluble lead salt formed a pale

yellow oil, which was distilled under diminished pressure. An analysis and the determination of its constants gave the following results:

0.1428 gave 0.4031 CO_2 and 0.1437 H_2O . $\text{C} = 77.0$; $\text{H} = 11.2$.

$d_{20^\circ/20^\circ} = 0.9148$. Neutralisation value 200.9. Iodine value 184.7.

$\text{C}_{18}\text{H}_{31}\text{O}_2$ requires $\text{C} = 76.6$; $\text{H} = 12.1$ per cent. Neutralisation value = 198.9. Iodine value = 90.1.

$\text{C}_{18}\text{H}_{32}\text{O}_2$ requires $\text{C} = 77.1$; $\text{H} = 11.4$ per cent. Neutralisation value = 200.4. Iodine value = 181.4.

$\text{C}_{18}\text{H}_{30}\text{O}_2$ requires $\text{C} = 77.7$; $\text{H} = 10.8$ per cent. Neutralisation value = 201.8. Iodine value = 274.0.

In order to ascertain more definitely the nature of the unsaturated acids, 10 grams of the mixture were dissolved in alkali, and oxidised with a 1.5 per cent. solution of potassium permanganate. The chief product of the oxidation, when crystallised from water, separated in thin needles, melting at $156-157^\circ$:

0.0630 gave 0.1426 CO_2 and 0.0594 H_2O . $\text{C} = 61.7$; $\text{H} = 10.5$.

$\text{C}_{18}\text{H}_{36}\text{O}_6$ requires $\text{C} = 62.1$; $\text{H} = 10.3$ per cent.

This substance was evidently tetrahydroxystearic acid (sativic acid). In addition to the latter acid, very small quantities of dihydroxystearic acid (m. p. 130°), linic acid (m. p. $200-205^\circ$), and isolinic acid (m. p. $173-174^\circ$) were obtained.

The above results would therefore indicate that the unsaturated acids consisted chiefly of linolic acid, with smaller amounts of oleic, linolenic, and isolinolenic acids.

Ethereal Extract of the Resin.

This extract was a black, brittle solid, and amounted to 19 grams. It was digested with 500 c.c. of ether, when the greater portion passed into solution, while a small amount of a light green powder remained undissolved. The latter was collected, and boiled with alcohol, in which it was very sparingly soluble, in order to remove the green colouring matter. It was finally crystallised from a mixture of pyridine and alcohol, when it separated in colourless needles, melting and decomposing at about 230° . It yielded an acetyl derivative, melting at 166° , which was analysed:

0.0854 gave 0.2142 CO_2 and 0.0690 H_2O . $\text{C} = 68.4$; $\text{H} = 9.0$.

$\text{C}_{22}\text{H}_{34}\text{O}_4(\text{CO}\cdot\text{CH}_3)_2$ requires $\text{C} = 68.8$; $\text{H} = 9.2$ per cent.

The above-described substance, when dissolved in chloroform with a little acetic anhydride, and a drop of concentrated sulphuric acid subsequently added, gave a pink coloration, rapidly changing to blue, and finally to green. It was evidently identical with the

dihydric alcohol designated as trifoliarol, which these alcohols have been isolated from the petroleum extract of the resins, which is

The above-mentioned ethereal solution of the extract was shaken successively with aqueous ammonium carbonate, and sodium hydroxide, and the various extracts obtained were separately examined. The ammonium trifoliarol removed only traces of a green resin. The first sodium extract yielded, on acidification, a dark green resin, which chiefly of chlorophyll, whilst the subsequent sodium extract, when acidified, gave a nearly colourless precipitate, which was collected and dissolved in alcohol, when a small amount of a substance separated in colourless, talon-like needles, melting at 253° . This substance was found to be identical with the substance designated as pratol, $C_{16}H_{12}O_4$, which had previously been isolated from the portion of the alcoholic extract of clover flower which was soluble in water. The mother liquors from the crystals of the pratol deposited a little of a crystalline substance, melting somewhat indefinitely between 178° and 183° , but the amount was too small to permit of its further examination. The final extraction of the ethereal liquid with sodium hydroxide yielded nothing but amorphous products, and on subsequently evaporating the ether only traces of a soft resin remained.

Chloroform and Ethyl Acetate Extracts of the Resin.

These extracts were black, brittle solids. They were small in amount, and nothing crystalline could be isolated from them.

Alcohol Extract of the Resin.

This was a dark brown, brittle solid, amounting to 43 grams. In order to ascertain whether it contained anything glucosidic, it was heated for some time with a 5 per cent. solution of sulphuric acid in aqueous alcohol, and the mixture subsequently distilled with steam, but no volatile oil or acid passed over. The distillation flask then contained, besides the aqueous liquid, a quantity of a black resin, which was collected and examined, but nothing definite could be isolated from it. The aqueous liquid, on the other hand, when extracted with ether, yielded a small quantity of a viscid, yellow oil, which gradually deposited a solid substance. The latter was crystallised from alcohol, when it separated in colourless needles, melting at 250° , and gave an acetyl derivative melting at 166° . This was found to be identical with the previously described substance, designated as pratol. The aqueous liquid

had been extracted with ether as above described, was freed from sulphuric acid by means of baryta, and concentrated to a small volume. It then readily reduced Fehling's solution, and yielded a small quantity of an osazone, melting at 203° . These facts indicated the presence of a glucoside in the alcoholic extract of the resin, and it is probable that the small amount of $C_{16}H_{12}O_4$, obtained from the latter represents one of its hydrolytic products.

Summary.

The detailed results of the present investigation of red clover flowers (*Trifolium pratense*, Linné) may be summarised as follows:—A quantity of the alcoholic extract, representing 37.1 kilograms of the dried flowers, when distilled with steam, yielded 10.5 grams, or 0.028 per cent., of essential oil. This essential oil, which contained furfuraldehyde, possessed the following constants: $n_D^{20} = 0.9476$; $\alpha_D + 4^{\circ}$ in a 1-dm. tube.

The portion of the alcoholic extract which was soluble in water contained a large amount of sugar, which yielded *d*-phenylglucosazone (m. p. 205°), but from the aqueous liquid the following definite substances were isolated: salicylic and *p*-coumaric acids;isorhamnetin, $C_{16}H_{12}O_7$ (m. p. 295°), which was probably present in the form of a glucoside; a number of new phenolic substances: *pratol*, $C_{15}H_8O_2(OH)(OCH_3)$, m. p. 253° , which apparently is a hydroxymethoxyflavone, and yields an *acetyl* derivative melting at 166° ; *pratensol*, $C_{17}H_9O_2(OH)_3$, m. p. 210° , which yields a *triacetyl* derivative melting at 189° ; a *yellow* compound, $C_{16}H_{10}O_7$ (m. p. 280°), which yields a *tetra-acetyl* derivative melting at 145 – 147° ; a *substance*, $C_{15}H_7O_3(OH)_3$, m. p. 225° , which yields a *triacetyl* derivative melting at 209° ; a *substance*, $C_{14}H_{12}O_6$ (m. p. 214°); also the following new glucosides: *trifolin*, $C_{22}H_{22}O_{11}, H_2O$ (m. p. 260°), which yields on hydrolysis a yellow colouring matter, *trifolitin*, $C_{16}H_{10}O_6$ (m. p. 275°), and rhamnose, $C_6H_{12}O_5$; *isotrifolin*, $C_{22}H_{22}O_{11}$ (m. p. 250°), and a glucoside of quercetin, melting at 235° .

The portion of the alcoholic extract which was insoluble in water consisted chiefly of resinous material, the amount of which was equivalent to 5.6 per cent. of the weight of dried clover flowers. From the resin the following compounds were obtained: myricyl alcohol, $C_{31}H_{63}OH$; heptacosane, $C_{27}H_{56}$, and hentriacontane, $C_{31}H_{64}$; sitosterol, $C_{27}H_{46}O$ (m. p. 135 – 136° ; $[\alpha]_D - 34.4^{\circ}$); a new dihydric alcohol, *trifolianol*, $C_{31}H_{64}O_2(OH)_2$ (m. p. 295°), which appears to be a homologue of ipuranol, $C_{23}H_{38}O_2(OH)_2$, and yields a *diacetyl* derivative melting at 165 – 166° and having $[\alpha]_D - 25.7^{\circ}$; a mixture of fatty acids, consisting chiefly of palmitic, stearic, and

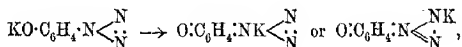
linolic acids, with small amounts of oleic, linolenic, and isolinolenic acids. A small amount of pradol, $C_{16}H_{32}O_4$, was likewise obtained, the latter having evidently been present in the resin in the form of a glucoside.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

XXVII.—*The Triazo-group. Part XII. Derivatives of*
para-Triazobenzaldehyde.

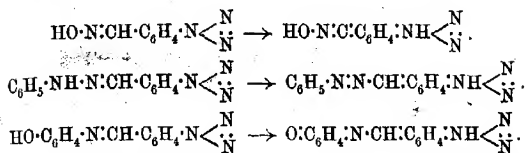
By MARTIN ONSLOW FORSTER and HILDA MARY JUDD.

AN investigation of the hydroxyphenylazoimides (Trans., 1907, 855 and 1350) brought to light a characteristic distinction between the potassium derivative of the para-compound and those of the ortho- and meta-triazophenols depending on the change of colour which takes place when the solution in water or absolute alcohol is heated; as a consequence of this treatment, the colourless substance is transformed into a dark blue material, which appears to be isomeric with its generator. The explanation of this behaviour which suggested itself at the time depends on the possibility of rearrangement having taken place in accordance with the following formulae:



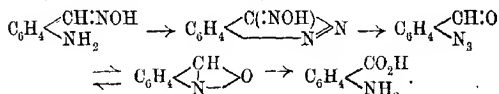
and although it was not possible to recognise any substantial difference between the acyl derivatives prepared from the blue compound and those obtained from the colourless potassium salt, they were certainly more highly coloured; moreover, whilst the *p*-triazophenol liberated from it by acids appears to have the general properties of the original material, the solid potassium derivative regenerated by the action of alkali is not colourless, but bluish-green.

The absence of any similar colour change in the case of ortho- and meta-hydroxyphenylazoimides has led us to examine certain para-derivatives of triazobenzene in which the occurrence of hydrogen in the group occupying the para-position afforded an opportunity of rearrangement on the lines indicated above. The condensation products from *p*-triazobenzaldehyde with hydroxylamine, phenylhydrazine, and *p*-aminophenol might have been expected, under favourable circumstances, to yield coloured modifications depending on transposition of hydrogen:

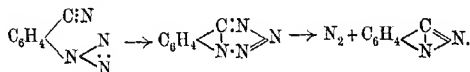


In no case, however, has any indication of a colour change by alkali been observed, and although it certainly happens that a chloroform solution of *p*-triazobenzaldehydephenylhydrazone rapidly becomes brown and ultimately purple when exposed to light, the observations of Chattaway (*Trans.*, 1906, **89**, 462) in connexion with the alteration which benzaldehydephenylhydrazone undergoes, would suggest correspondence between the two phenomena.

There does not appear to be any tendency on the part of the triazo-group in *p*-triazobenzaldehyde to enter into association with the aldehyde radicle in the manner brought to light by Bamberger and Demuth (*Ber.*, 1901, **34**, 1309) during an investigation of certain ortho-aminobenzaldoximes. These authors found that on diazotising *o*-aminobenzaldoxime there is produced indiazoneoxime, isomeric with *o*-triazobenzaldehyde, into which it passes on treatment with alkali or warm water; furthermore, they showed that *o*-triazobenzaldehyde may be converted readily into anthranilic acid through anthranil, from which they regenerated it by the combined action of hydroxylamine and oxygen (*loc. cit.*, 3874 and 4015):



As the production of anthranil from *o*-triazobenzaldehyde must depend on an opening of the azoimide ring analogous to that incurred by diazomethane when this compound transforms aldehydes into ketones (Schlotterbeck, *Ber.*, 1907, **40**, 479; 1909, **42**, 2559), it seemed reasonable to expect a similar transformation in the case of *o*-triazobenzonitrile:



The substance in question was therefore prepared by the action of hydrazoic acid on *o*-cyanobenzediazonium chloride; it was found that alkali, however, which transforms *o*-triazobenzaldehyde into anthranilic acid with loss of nitrogen, leaves the triazo-group in *o*-triazobenzonitrile intact, the substance being merely hydrolysed to

o-triazobenzoic acid. During this process there does not occur any elimination of the triazo-group in the form of alkali azide, and the same power of resistance is displayed by the triazo-group in *p*-triazobenzaldoxime. These observations are of some interest in connexion with the effect produced by other groups on the tenacity with which the azoimide complex is held by the benzene ring. Noeltling, Grandmougin, and Michel (*Ber.*, 1892, 25, 3328) were the first to show that a nitro-group in the ortho- or para-position unloosed the triazo-group, which remained indifferent to the presence of methyl and the meta-nitro-complex; a similar relationship was found applicable to the naphthalene series (Forster and Fierz, *Trans.*, 1907, 91, 1942), with the addition that a heteronuclear nitro-group in the 5:1, 8:1, 5:2, and 8:2 positions left the azoimide radicle unaffected by alkali. Furthermore it was shown (*loc. cit.*, 1356) that boiling potassium hydroxide solution eliminates 20 per cent. of hydrazoic acid from *p*-hydroxyphenylazoimide without yielding a trace of this product from the ortho-derivative.

We have taken this opportunity to study the relationship of the oximes obtainable from *p*-triazobenzaldehyde, and find that the production and properties of these substances are governed by the same generalisations which prevail among their better known analogues. The *anti*-aldoxime, melting at 98°, is the direct product of treating the aldehyde with hydroxylamine, and is converted by the action of hydrogen chloride in dry ether into the *syn*-aldoxime, which melts at 142°. The latter modification is labile, being transformed into the more fusible isomeride at 100°, and on treatment with benzoyl chloride in pyridine yields the same benzoyl derivative as that obtained from the *anti*-aldoxime; the *p*-triazobenzaldoximes thus resemble the unsubstituted compounds, from which only one benzoyl derivative is obtainable. On consulting the literature we found that the benzoyl derivative of benz-*anti*-aldoxime was produced by direct action of benzoyl chloride (Minunni and Corselli, *Gazzetta*, 1892, 22, ii, 167), and consequently in presence of hydrogen chloride. Nevertheless we have failed to obtain an isomeric benzoyl derivative under modified conditions, the only product arising by the action of benzoyl chloride on the dry sodium derivative of both benzaldoximes in ether consisting of the substance melting at 101° described by Minunni and Corselli; benzoylation in dry pyridine or in presence of aqueous alkali was equally unsuccessful. The benzoyl derivative of *p*-triazobenzaldoxime is readily decomposed into *p*-triazobenzonitrile and benzoic acid, and on attempting to prepare the *p*-toluenesulphonyl derivative, this nitrile was the sole recognisable product. From the sodium derivative of benz-*anti*-aldoxime, however, a very unstable *p*-toluenesulphonyl compound has been prepared, melting at 88°, and

undergoing decomposition into benzonitrile at the laboratory temperature; the *syn*-aldoxime did not yield a *p*-toluenesulphonyl derivative, however, even when exactly the same conditions were observed, benzonitrile alone being formed, and it is noteworthy in this connexion that the nitrile was produced from both oximes by the action of benzenesulphonyl chloride in pyridine (Werner and Piguet, *Ber.*, 1904, 37, 4308). β -Naphthalenesulphonyl chloride appears to be incapable of attacking the isomeric benzaldoximes and their *p*-triazio-derivatives in pyridine at zero.

EXPERIMENTAL.

The p-Triazobenzaldoximes, $N_2 \cdot C_6H_4 \cdot CH \cdot NOH$.

The *p*-triazobenzaldehyde required for the preliminary experiments was prepared by the action of sodium carbonate on a solution of diazotised *p*-aminobenzaldehyde to which hydroxylamine hydrochloride had been added (Rupe and von Majewski, *Ber.*, 1900, 33, 3401), but we subsequently obtained a more satisfactory product by the following process.

Fifty grams of finely powdered *p*-aminobenzaldehyde were mixed with crushed ice, stirred with 150 c.c. of concentrated hydrochloric acid, and diazotised with 25 grams of sodium nitrite in the minimum of water; after half an hour some carbamide was added, and the liquid filtered rapidly from tar. The ice-cold diazonium salt, now clear and orange-yellow, was treated with 20 grams of sodium azide, added gradually in aqueous solution; brisk evolution of nitrogen occurred, and the triazobenzaldehyde separated in the form of a pale brown oil, which, after an hour, was extracted with ether, shaken twice with 10 per cent. hydrochloric acid, and dried with calcium chloride, thereby losing much of the brown impurity. The triazobenzaldehyde weighed 32 grams.

p-Triazobenz-anti-aldoxime was prepared by adding 6 grams of hydroxylamine hydrochloride to 5 grams of the aldehyde suspended in 50 c.c. of 15 per cent. potassium hydroxide, the characteristic odour of *p*-triazobenzaldehyde, which recalls anise, being no longer perceptible after half an hour. Carbon dioxide was then passed through the liquid, and the deep brown precipitate recrystallised from dilute alcohol, forming lustrous plates which melt at 98°:

0.1119 gave 33 c.c. N_2 at 16° and 769 mm. $N = 34.80$.

$C_7H_6ON_4$ requires $N = 34.56$ per cent.

The substance is freely soluble in methyl and ethyl alcohols, ethyl acetate, chloroform, ether, glacial acetic acid, acetone, or carbon tetrachloride; benzene dissolves it less readily, and petroleum

sparingly, depositing it in flat, pale yellow needles. It is volatile in steam, and when crystallised from boiling water is practically colourless. Ether extracts small quantities from solutions in alkali hydroxide. When exposed to light the substance rapidly becomes dark brown, but there is no change of colour when a solution in 50 per cent. potassium hydroxide is boiled, unaltered material being recovered on acidification; moreover, one gram of the substance was heated with 20 per cent. aqueous potassium hydroxide during four hours on the water-bath without yielding a trace of potassium azide. Torrents of gas were liberated by concentrated sulphuric acid, which formed a dark brown liquid indifferent towards Fehling's solution. Stannous chloride in hydrochloric acid also sets free gas, yielding a bright red solution, from which a dark reddish-brown precipitate quickly separated; this material, probably an azo-compound, is insoluble in benzene, but dissolves in alcohol, the deep red solution becoming yellow with alkali and having its red colour restored by acids.

The *methyl ether* was obtained by the silver oxide method as a colourless oil having a powerful odour of anise, and also arises by the action of diazomethane on a solution of the oxime in dry ether (Forster and Dunn, Trans., 1909, 95, 425); it is readily volatile in steam, and is not dissolved by alkalis.

p-Triazobenz-syn-aldoxime arose in the form of hydrochloride on passing dry hydrogen chloride into a solution of the *anti*-oxime (m. p. 98°) in ether. The salt, after being washed with ether, was suspended in this medium and decomposed with sodium carbonate, the ethereal solution of the *syn*-oxime being then dried by sodium sulphate and evaporated at the laboratory temperature. The colourless, crystalline residue was recrystallised from warm benzene, which deposited a felted mass of very pale yellow, silky needles:

0.0498 gave 14.2 c.c. N_2 at 10.5° and 775 mm. $N = 34.64$.

$C_7H_6ON_4$ requires $N = 34.56$ per cent.

The melting point, 142°, is sharp, although the substance decomposes. The oxime is readily soluble in methyl and ethyl alcohols, from which water precipitates lustrous, slender needles; it is freely soluble in cold ethyl acetate, chloroform, ether, acetone, or glacial acetic acid, but is only sparingly so in benzene, and almost insoluble in light petroleum. It resembles the more fusible isomeride in being very sensitive to light, volatile in steam, and extractable by ether from its alkaline solutions. Unlike the *syn*-modification of benzaldoxime and its nitro-derivatives, the triazo-compound appears to resist any tendency to undergo transformation into the *anti*-form on recrystallisation, and must be heated for several minutes at 100° before the

isomeride is regenerated; the *syn*-oxime may even be recovered unchanged from a solution in 10 per cent. potassium hydroxide which has been heated in steam during fifteen minutes.

Action of Acyl Chlorides on the Oximes.—On mixing pyridine solutions containing 1.4 grams of benzoyl chloride and 1.6 grams of the *anti*-aldoxime, the temperature rose, and the liquid was therefore surrounded with melting ice during one hour, and afterwards poured into cold water; the oil precipitated in this manner became semi-solid on treatment with dilute acetic acid, and after being rubbed with a few drops of cold alcohol and drained on earthenware, yielded a colourless solid, only moderately soluble in alcohol, from which it crystallised in minute, lustrous needles melting at 146° with decomposition:

0.1325 gave 23.5 c.c. N_2 at 11° and 758 mm. $N = 21.12$.

$C_{14}H_{10}O_2N_4$ requires $N = 21.05$ per cent.

On proceeding in exactly the same way with the *syn*-aldoxime, the product is identical.

It was noticed that if the oil which is precipitated on pouring the pyridine solution into water is allowed to remain in the liquid without adding acetic acid, the benzoyl derivative disintegrates in the course of a few days, yielding *p*-triazobenzonitrile, a specimen of which, after crystallisation from alcohol, melted at 71°, and was therefore identical with the substance obtained by Rupe and von Majewski (*loc. cit.*, 3406) from *p*-cyanobenzenediazonium perbromide and ammonia.

The action of *p*-toluenesulphonyl chloride in pyridine was also studied, and with this agent both oximes were converted into the nitrile. β -Naphthalenesulphonyl chloride, however, appears to be devoid of action, unchanged material being recovered in each case when the isomeric oximes were treated with this compound in pyridine.

Action of Potassium Cyanide on p-Triazobenzaldehyde.

In preparing *p*-triazobenzaldehyde by the process of Rupe and von Majewski, we were led to suspect the occurrence of a subsidiary action indicated by the comparative indifference of the product towards hydroxylamine and phenylhydrazine. As it seemed possible that a portion of the aldehyde had become converted into bis-*p*-triazobenzoin, we attempted to compare this compound by the action of potassium cyanide, but it was soon evident that this agent, instead of effecting benzoin synthesis, had attacked the triazo-group in the manner described by Wolff and Lindenhayn (*Ber.*, 1904, 37, 2374), giving rise to the potassium derivative of the corresponding triazen,
 $OCH \cdot C_6H_4 \cdot N \cdot N \cdot NK \cdot CN$.

Ten grams of the aldehyde in 20 c.c. of absolute alcohol were heated with 2 grams of potassium cyanide in 10 c.c. of water during half an hour under reflux; the liquid deposited a small quantity of potassium cyanide as it cooled, and when filtered from this was allowed to evaporate spontaneously. Bright yellow crystals were obtained embedded in oil, and on recrystallisation from alcohol formed radial groups of long, pale yellow prisms:

0.0435 gave 0.0179 K_2SO_4 . $K = 18.40$.

$C_8H_6ON_4K$ requires $K = 18.40$ per cent.

The salt has not a definite melting point, decomposing at a high temperature with extensive intumescence; it is readily soluble in water, the yellow colour of the solution being destroyed by hydrochloric acid and restored by alkali.

p-Triazobenzaldehydephenylhydrazone, $N_8 \cdot C_6H_4 \cdot CH:N \cdot NH \cdot C_6H_5$.

On mixing 4 grams of *p*-triazobenzaldehyde with 3 grams of phenylhydrazine, water separated immediately, the liquid became hot, and solidified on cooling; the product was recrystallised from methyl alcohol, followed by petroleum, which deposited minute, straw-coloured needles melting at 190° without evolving gas, although steady effervescence began at 120° :

0.1103 gave 28.2 c.c. N_2 at 17° and 767 mm. $N = 29.95$.

$C_{13}H_{11}N_8$ requires $N = 29.53$ per cent.

The phenylhydrazone is freely soluble in cold acetone, benzene, ethyl acetate, and chloroform, the solution in the last named becoming deep brown and ultimately purple when exposed to light; this colour change has not been observed in the case of any other medium, and recalls the observations of Chattaway in connexion with benzaldehydephenylhydrazone (*loc. cit.*). Concentrated sulphuric acid develops a transient, intense blue coloration, followed immediately by liberation of gas; this was also set free by stannous chloride in hydrochloric acid, which ultimately gives rise to a deep reddish-brown precipitate. There is not any change of colour when the substance is heated with concentrated potash in either alcohol or water.

p-Triazobenzaldehyde-*p*-aminophenol, $N_8 \cdot C_6H_4 \cdot CH:N \cdot C_6H_4 \cdot OH$.

Five grams of *p*-aminophenol hydrochloride in water were mixed with 5 grams of sodium acetate and shaken with 5 grams of *p*-triazobenzaldehyde, when the emulsion was transformed into a paste of crystals; after recrystallisation from benzene, the substance was

obtained in lustrous, golden-brown, six-sided plates, melting at 175° with vigorous intumescence.

0.1378 gave 27.5 c.c. N_2 at 14° and 765.5 mm. $N = 23.64$.

$C_{15}H_{10}ON_4$ requires $N = 23.53$ per cent.

The substance is moderately soluble in boiling methyl alcohol, but only sparingly soluble in boiling benzene, and insoluble in boiling petroleum; acetone and ethyl acetate dissolve it readily when warm, depositing the substance in clear-cut, hexagonal prisms, whilst boiling chloroform dissolves it sparingly. When suspended in water and heated with potassium hydroxide, the deep yellow solution of the potassium derivative quickly deposits lustrous crystals, but the sparingly soluble product undergoes no colour change when heated with concentrated potash, aqueous or alcoholic. The substance is decomposed immediately by concentrated sulphuric acid, liberating gas, which is also set free by stannous chloride in hydrochloric acid, the deep red solution rapidly depositing a dark reddish-brown precipitate.

Condensation of p-Triazobenzaldehyde with Camphoryl- ψ -semicarbazide.

Four grams of camphoryl- ψ -semicarbazide nitrate dissolved in water were warmed with two grams of *p*-triazobenzaldehyde, when the liquid became turbid and colourless needles separated. The highly insoluble product was exhausted with a small quantity of boiling absolute alcohol, and then dissolved in a large proportion of boiling acetone; dilution with water led to the separation of transparent, pale yellow, rectangular prisms, infusible below 250° , although suddenly becoming brown at about 200° :

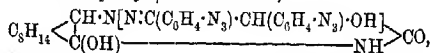
0.1287 gave 0.2948 CO_2 and 0.0587 H_2O . $C = 62.45$; $H = 5.06$.

0.1371 „ 30.8 c.c. N_2 at 15° and 763 mm. $N = 26.46$.

$C_{18}H_{20}O_2N_6$ requires $C = 61.00$; $H = 6.21$; $N = 23.73$ per cent.

$C_{25}H_{26}O_2N_9$ „ $C = 62.11$; $H = 5.17$; $N = 26.09$ „ „

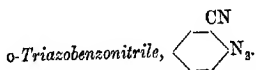
The constitution of the product is somewhat obscure. The analytical results are not in agreement with the empirical formula $C_{18}H_{20}O_2N_6$, that of *p*-triazobenzaldehyde camphoryl- ψ -semicarbazone, and are equally incompatible with the anhydride, which, in view of the readiness with which camphoryl- ψ -semicarbazide loses $1H_2O$, might possibly have arisen. The formula indicated is that of bis-*p*-triazobenzoin camphoryl- ψ -semicarbazone,



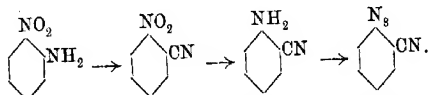
less $1H_2O$, an expression which gains probability from the infusibility of the substance, because the camphoryl- ψ -semicarbazones

already described (Trans., 1905, 87, 727) melt below 250° , whilst the anhydride of camphoryl-*p*-semicarbazide is not fused until 280° is reached.

A solution containing 0.1745 gram in 25 c.c. of chloroform gave $n_D^{20} 7^{\circ}46'$ in a 2-dm. tube, whence $[\alpha]_D^{20} 556.3^{\circ}$, whilst a pyridine solution with 0.2600 gram in 25 c.c. gave $n_D^{20} 0^{\circ}30'$ for the same length, corresponding with $[\alpha]_D^{20} 24.0^{\circ}$.



The azoimide was produced by the following steps from *o*-nitroaniline:



Adopting the modification of Sandmeyer's method, described by Pinnow and Müller (*Ber.*, 1895, 28, 151), we found that the *o*-nitrobenzonitrile was more conveniently separated from the uninviting product of treatment with cuprous cyanide by allowing the black mass to become dry, extracting it with chloroform, and adding petroleum to the filtered liquid; in this way, 50 grams of *o*-nitroaniline furnished 37 grams of *o*-nitrobenzonitrile in crystalline form. The difficulties which beset the reduction of *o*-nitrobenzonitrile to *o*-aminobenzonitrile have been already described by Pinnow and Müller (*loc. cit.*; compare also Reissert and Grube, *Ber.*, 1903, 42, 3710), and we isolated the hydrochloride of the base in the manner indicated by them, removing the associated hydrochloride of *o*-aminobenzamide by treatment with cold water.

Fifteen grams of *o*-aminobenzonitrile hydrochloride were suspended in 80 c.c. of hydrochloric acid and diazotised with 25 grams of sodium nitrite; by using a larger proportion of hydrochloric acid than that employed by Pinnow and Samann (*Ber.*, 1896, 29, 630), the formation of *o*-dicyanodiazaminobenzene, which represented 80 per cent. of the theoretical amount in their experiment, was almost entirely avoided, and the filtered diazonium salt gave *o*-triazobenzonitrile in the form of a colourless precipitate on adding 20 grams of sodium azide. The dried product was recrystallised from petroleum (b. p. $60-80^{\circ}$), which deposits pale yellow, lustrous leaflets, quickly becoming brown when exposed to light; it sinters at 51° and is completely fused at 58° :

0.0792 gave 27.0 c.c. N_2 at 17° and 748 mm. $N = 38.92$.

$C_7H_4N_4$ requires $N = 38.88$ per cent.

The substance is freely soluble in cold chloroform, ethyl acetate, benzene, or acetone, readily so in alcohol, and more sparingly so in hot petroleum. Although the solid material is odourless, the vapour in steam has a penetrating odour, without suggestion of anise. There is violent decomposition with concentrated sulphuric acid.

Action of Alcoholic Potash.—An alcoholic solution of *o*-triazobenzo-nitrile was heated two hours under reflux with potassium hydroxide dissolved in the minimum quantity of water. Nitrogen was not set free, and on evaporating the solution, potassium azide could not be detected in the residue, which was then dissolved in water and treated with dilute sulphuric acid. The precipitated *o*-triazobenzoic acid was recrystallised from boiling water, from which it separated in minute, lustrous needles, melting and decomposing at 146° ; analysis gave 25.97 per cent. of nitrogen, 25.76 and 34.57 per cent. being required by the formulæ $C_7H_3O_3N_3$ (triazobenzoic acid) and $C_7H_4ON_4$ (triazobenamide) respectively, and the acid is therefore identical with the one obtained by Griess from anthranilic acid (*Zeitsch. für Chem.*, 1867, 165) and by Bamberger and Demuth (*Ber.*, 1901, 34, 1337) from *o*-triazobenzaldehyde.

Action of Acyl Chlorides on the Isomeric Benzaldoximes.

So far as we have been able to ascertain, the only benzoyl derivative of benzaldoxime is that described by Minunni and Corselli (*loc. cit.*), who prepared it from benz-*anti*-aldoxime and benzoyl chloride in dry ether. In view of the existence of two acetyl derivatives corresponding with the *anti*- and *syn*-aldoximes, it appeared worth while to attempt the production of a benzoyl derivative from benz-*syn*-aldoxime under conditions excluding the presence of free hydrogen chloride.

As a preliminary experiment, the sodium derivative of benz-*anti*-aldoxime suspended in dry ether was treated with the calculated amount of benzoyl chloride, the very vigorous action which ensued being checked by surrounding ice and water; after half an hour, anhydrous sodium carbonate was added to destroy any slight excess of benzoyl chloride, when the filtered solution deposited the known benzoyl derivative melting at 101° . On treating the sodium derivative of benz-*syn*-aldoxime in precisely the same way, the same substance was produced, no depression of melting point occurring on admixture.

An attempt to prepare a *p*-toluenesulphonyl derivative of benz-*anti*-aldoxime by the same process was unsuccessful; the residue left by the solvent remained liquid, and decomposed explosively on slightly raising the temperature, when torrents of gas were liberated, whilst

the tarry residue had the odour of phenylcarbylamine. On shaking the sodium derivative of benz-*anti*-aldoxime with *p*-toluenesulphonyl chloride in 5 per cent. sodium hydroxide during two and a-half hours, a strong odour of benzonitrile was developed, and a small proportion of a solid substance remained undissolved; after crystallisation from light petroleum, this melted at 88°, and was prepared more conveniently by rubbing the sodium derivative with *p*-toluenesulphonyl chloride and weak sodium carbonate solution. After remaining twenty-four hours in the ice-chest, the pasty mass, with the odour of phenylcarbylamine, had become brittle, and, when washed with sodium carbonate and dried in the desiccator, was dissolved in cold benzene, from which petroleum precipitated it in lustrous, colourless prisms melting with profound decomposition at 88°:

0.5359 gave 24.6 c.c. N₂ at 24° and 758 mm. N = 5.15.

C₁₄H₁₈O₃NS requires N = 5.09 per cent.

The substance is highly unstable, even when purified, especially if kept in a stoppered bottle, undergoing decomposition after forty-eight hours in daylight to a tarry mass which has the odour of benzonitrile; a specimen on a watch-glass in a large desiccator protected from light, however, remained many months without alteration.

On proceeding in the same way with benz-*syn*-aldoxime, the only product was benzonitrile, and on substituting β -naphthalenesulphonyl chloride for the toluene derivative, there did not appear to be any action with either oxime.

ROYAL COLLEGE OF SCIENCE, LONDON.
SOUTH KENSINGTON, S.W.

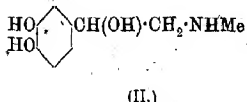
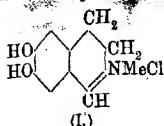
XXVIII.—*isoQuinoline Derivatives. Part IV. ortho-Dihydroxy-bases. The Conversion of 1-Keto-6:7-dimethoxy-2-alkyltetrahydroisoquinolines into 3:4-Dihydroxyphenylethylalkylamines.*

By FRANK LEE PYMAN.

In the preceding papers of this series (Trans., 1909, 95, 1266, 1610, 1738) a number of 6:7-dimethoxyisoquinoline derivatives have been described. Some of these proved to be physiologically active substances, and it was thought likely that the corresponding 6:7-dihydroxy-bases might be compounds of still more marked physiological action.

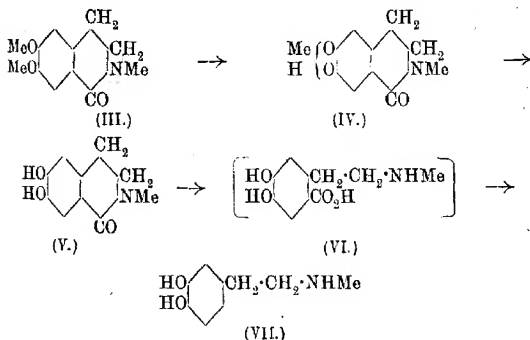
In particular, it seemed possible that compounds of this type, such, for instance, as 6:7-dihydroxy-2-methyl-3:4-dihydroisoquinolinium chloride (I), might produce a pressor effect similar to that caused by

3:4-trihydroxyphenylethylmethylamine (II), the *levo*-modification of which is the active principle of the suprarenal gland, since they would be in some respects similarly constituted:

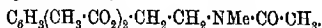


With this object in view, several dimethoxyisoquinoline derivatives have been converted by treatment with hydrochloric acid into the corresponding dihydroxy-bases, which were then submitted to physiological examination, but in no case where the isoquinoline ring remained intact had the resulting dihydroxy-base any marked pressor properties. It was found, however, that the 1-keto-6:7-dimethoxy-2-alkyltetrahydroisoquinolines, when treated with hydrochloric acid at a sufficiently high temperature, gave rise to bases of considerable pressor properties, in which the isoquinoline ring was no longer preserved.

Thus, when 1-keto-6:7-dimethoxy-2-methyltetrahydroisoquinoline (III) is heated with hydrochloric acid under pressure for three hours at 175°, it is quantitatively converted into the hydrochloride of 3:4-dihydroxyphenylethylmethylamine (VII). By working at temperatures lower than 175°, however, two immediate products, 7(or 6)-hydroxy-1-keto-6(or 7)-methoxy-2-methyltetrahydroisoquinoline (IV) and 6:7-dihydroxy-1-keto-2-methyltetrahydroisoquinoline (V), may be isolated, and it is therefore evident that the mechanism of the change at 175° consists in the successive hydrolysis of the two methoxyl groups, followed by hydration of the lactam, forming the corresponding amino-acid (VI), and subsequent decomposition of the latter into carbon dioxide and the amine. The course of the reaction may therefore be represented by the following scheme:

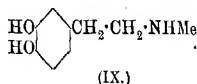
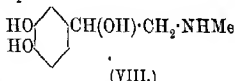


It may be pointed out that the ring fission illustrated above is precisely similar to that occurring in the formation of 8-aminovaleric acid from α -piperidone (Schotten, *Ber.*, 1888, 21, 2242), whilst the loss of carbon dioxide from the resulting acid is a not uncommon property of hydroxybenzoic acids when under the influence of hydrochloric acid at a high temperature. Proof of the presence of an imino-group in the final product is afforded by the fact that it yields a neutral triacetyl derivative,



It was found that on increasing the size of the alkyl group on the nitrogen atom, the ring fission and subsequent elimination of carbon dioxide took place with greater difficulty; thus, under the conditions (three hours at 175°) which sufficed to convert 1-keto-6:7-dimethoxy-2-methyltetrahydroisoquinoline almost completely into 3:4-dihydroxyphenylethylmethylamine, the ethyl and propyl homologues were only partly converted into the corresponding 3:4-dihydroxyphenylethylalkylamines, the former giving 30 per cent. and the latter 79 per cent. of the theoretical yield of the corresponding 6:7-dihydroxy-1-keto-2-alkyltetrahydroisoquinoline.

The similarity of structure between the 3:4-dihydroxyphenylethylalkylamines and β -3:4-trihydroxyphenylethylmethylamine (VIII) is obvious; 3:4-dihydroxyphenylethylmethylamine (IX), in fact, differs only from this valuable drug in being devoid of the alcoholic hydroxyl group.



The physiological action of this compound (and of the others mentioned in this paper) has been examined by Dr. H. H. Dale of the Wellcome Physiological Research Laboratories, to whom the author is indebted for the following report:

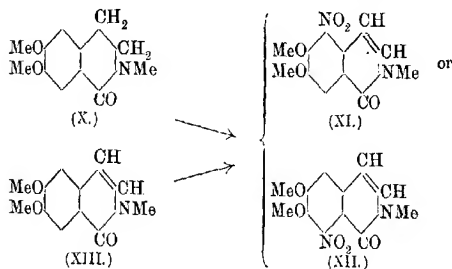
3:4-Dihydroxyphenylethylmethylamine has the characteristic suprarenal action in a high degree, being the nearest in action to the true active principle of any of the large series of related substances which Dr. Dale has now examined; qualitatively there is little difference in the action of the two on organs innervated by sympathetic nerves. The characteristic rise of blood-pressure; acceleration and augmentation of the heart's action; contraction of the pregnant and inhibition of the non-pregnant uterus of the cat; dilatation of the pupil; secretion of saliva—all are produced. A 1 in 1000 solution produced marked and sustained pallor of the conjunctival mucous membrane when instilled into the eye.

Quantitatively, by finding doses which produce rises of blood-

pressure to equal submaximal heights,* Dr. Dale has found that 3:4-dihydroxyphenylethylmethylamine has an activity approximately one-seventh of that of racemic β -3:4-trihydroxyphenylethylmethylamine, or one-tenth of that of the naturally-occurring *lavo*-modification.

The corresponding ethyl- and propyl-amines behave in a similar manner, but to a less extent, the ethylamine having about one-third and the propylamine less than one-twentieth of the activity of the methylamine.†

The valuable properties of 3:4-dihydroxyphenylethylmethylamine suggested the preparation of a trihydroxyphenylethylmethylamine, and it was proposed to prepare such a compound by nitrating 1-keto-6:7-dimethoxy-2-methyltetrahydroisoquinoline, reducing the nitro-compound, substituting a hydroxyl for the amino group in the usual way, and decomposing the product with hydrochloric acid. This synthesis seemed *a priori* promising, since Freund (*Ber.*, 1887, 20, 2406) has described a nitro-oxyhydrastinine obtained by the action of warm dilute nitric acid on oxyhydrastinine. Unfortunately, the action of this reagent on 1-keto-6:7-dimethoxy-2-methyltetrahydroisoquinoline (X) consisted not only in nitration, but also in simultaneous oxidation, two atoms of hydrogen being removed with the formation of a bright yellow nitro-compound having the formula $C_{12}H_{12}O_5N_2$. This proved to be 5(or 8)-nitro-1-keto-6:7-dimethoxy-2-methyl-1:2-dihydroisoquinoline ‡ (XI or XII), for it was readily obtained by nitrating 6:7-dimethoxy-*N*-methylisoquinolone (XIII) (1-keto-6:7



* The validity and limitations of this method of comparison will be shortly discussed elsewhere in a paper by Barger and Dale.

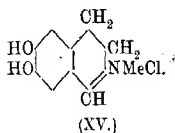
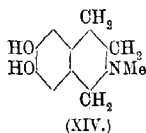
† The parent base, 3:4-dihydroxyphenylethylamine, will shortly be described in a communication to the Society by Barger and Ewins (compare *Trans.*, 1902, 95, footnote to p. 2194).

‡ In view of this result, and since the preparation and properties of this nitro-compound and Freund's "nitro-oxyhydrastinine" are precisely similar, it seems probable that the latter compound is in reality 5(or 8)-nitro-1-keto-6:7-methyl-enedioxy-2-methyl-1:2-dihydroisoquinoline.

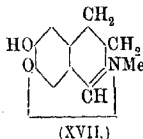
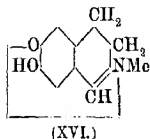
dimethoxy-2-methyl-1:2-dihydroisoquinoline), a compound prepared by Decker and Pschorr (*Ber.*, 1904, 37, 3401) by the oxidation of *N*-methylisopapaverine.

No further investigation of this compound was made, since 1-keto-2-alkyl-1:2-dihydroisoquinolines do not appear to become converted into phenylethylenealkylamines under the influence of acids at high temperatures; thus, 1-keto-2-methyl-1:2-dihydroisoquinoline can be quantitatively recovered unchanged after heating with hydrochloric acid under pressure for two hours at 170°.

Reference has already been made to the preparation of dihydroxy-bases containing the isoquinoline ring; these are readily obtained in good yield by the action of hydrochloric acid at 175° on the corresponding dimethoxy-compounds; 6:7-dihydroxy-2-methyltetrahydroisoquinoline (XIV) and 6:7-dihydroxy-2-methyl-3:4-dihydroisoquinolinium chloride (XV) have no decided physiological action:

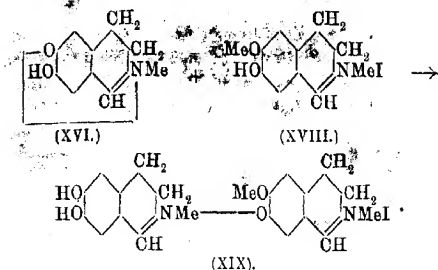


On the addition of sodium carbonate to a solution of the latter compound, the *phenolbetaine* of the corresponding isoquinolinium hydroxide is obtained. This compound has one of the two formulæ (XVI) or (XVII), but no attempt has been made to determine

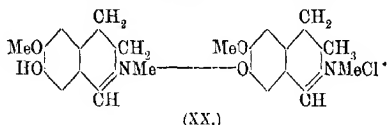


which of the two is correct, although for the purpose of further discussion the former has been arbitrarily adopted throughout this communication.

This base exhibits the characteristic properties of phenolbetaines (compare Decker and Dunant, *Annalen*, 1908, 358, 296), amongst others that of forming the iodide of the corresponding methoxy-compound, 7(or 6)-hydroxy-6(or 7)-methoxy-2-methyl-3:4-dihydroisoquinolinium iodide (XVIII), when heated with methyl iodide. At the same time, a compound (XIX) of the latter with one molecule of the phenolbetaine is found in accordance with the following scheme:



This compound may be crystallised unchanged, and can be converted into the chloride by means of silver chloride, and crystallised as such without breaking down, but is readily decomposed by hydriodic acid, the compounds from which it was formed being reproduced. Mixed external phenolbetaines of this type do not appear to have been previously observed, but simple external phenolbetaines of the type $\text{HO}\cdot\text{R}_1\text{N}-\text{O}-\text{R}_2\text{NI}$ have been obtained by Griess (*Ber.*, 1880, 13, 246) and by Claus and Howitz (*J. pr. Chem.*, 1890, [ii], 42, 222) and their collaborators by the action of ammonia on substituted ammonium iodides of the type $\text{HO}\cdot\text{R}_1\text{NI}$; a simple external phenolbetaine (XX) of this type can be similarly obtained from 7(or 6)-hydroxy-6(or 7)-methoxy-2-methyl-3:4-dihydroisoquinolinium chloride (XVIII).



EXPERIMENTAL.

1-Keto-6:7-dimethoxy-2-methyltetrahydroisoquinoline.

By the method of preparation of this compound by simultaneous oxidation and reduction of 4:5-dimethoxy-2- β -methylaminoethylbenzaldehyde (*Trans.*, 1909, 95, 1272), only one-half of the original material is transformed into the above substance. It can, however, be prepared in almost theoretical yield from the same material by the method devised by Freund (*Ber.*, 1889, 22, 457) for the conversion of hydrastinine into oxyhydrastinine, namely, by oxidation by permanganate in the presence of alkali.

Two grams of 6:7-dimethoxy-2-methyl-3:4-dihydroisoquinolinium chloride were dissolved in 180 c.c. of water, rendered alkaline by the addition of 20 c.c. of 10 per cent. aqueous sodium hydroxide, and

mixed with a solution of 0.8 gram (a slight excess) of potassium permanganate in 20 c.c. of water. After one hour, the solution was filtered from manganese dioxide, neutralised with dilute sulphuric acid, evaporated to low bulk, and extracted with ether. After evaporation of the solvent, 1.4 grams of pure 1-keto-6:7-dimethoxy-2-methyltetrahydroisoquinoline were obtained, that is, 96 per cent. of the theoretical.

To the description of this compound previously given (*loc. cit.*), the following may be added. It can be distilled under diminished pressure without decomposition, and passes over as a nearly colourless oil, which solidifies on cooling, at $244^{\circ}(\text{corr.})/16$ mm.

It is easily soluble in water, but, on agitating a strong aqueous solution, an unstable *hydrate* separates as a mass of silky needles, which are sparingly soluble in water. When this hydrate is collected and dried for half an hour on porous porcelain, it melts indefinitely at $40-70^{\circ}$, but on exposure to air for twelve hours becomes anhydrous, has the melting point $126^{\circ}(\text{corr.})$ of the anhydrous base, and is, as before, easily soluble in water.

5-(or 8)-Nitro-1-keto-6:7-dimethoxy-2-methyl-1:2-dihydroisoquinoline
(XI or XII, p. 267).

Ten grams of 1-keto-6:7-dimethoxy-2-methyltetrahydroisoquinoline were dissolved in a solution of 10 grams of concentrated nitric acid in 30 c.c. of water and heated on the water-bath. The liquor quickly became brown, and then effervesced vigorously with evolution of brown fumes, whilst a quantity of yellow needles continuously separated out. After a few minutes, the liquor was cooled, filtered from the separated crystals, and again heated, this time over a free flame, when a further quantity of crystals were obtained; these operations were again repeated after the addition of another 5 c.c. of concentrated nitric acid, until no further quantity of the crystalline compound could be obtained. The total yield amounted to 6.4 grams.

5-(or 8)-Nitro-6:7-dimethoxy-2-methyl-1:2-dihydroisoquinoline crystallises from glacial acetic acid in fine bright, canary-yellow needles, which begin to soften at about 240° and melt at $244-245^{\circ}(\text{corr.})$. It is easily soluble in chloroform, fairly easily so in boiling glacial acetic acid or xylene, but almost insoluble in water or the other usual organic solvents:

0.1521 gave 0.3032 CO_2 and 0.0611 H_2O . $\text{C} = 54.4$; $\text{H} = 4.7$.

$\text{C}_{12}\text{H}_{12}\text{O}_6\text{N}_2$ requires $\text{C} = 54.5$; $\text{H} = 4.6$ per cent.

Like Freund's "nitro-oxyhydrastinine" (*loc. cit.*), it is insoluble in dilute acids or weak alkalis, but dissolves in warm aqueous sodium

hydroxide, and is reprecipitated in a gelatinous form on the addition of dilute acids.

The same nitro-compound is readily obtained by warming 1 gram of 1-keto-6:7-dimethoxy-2-methyl-1:2-dihydroisoquinoline with a mixture of 1 c.c. of concentrated nitric acid and 3 c.c. of water; the identity of the product of this reaction with that described above follows from the fact that the two products and a mixture of both melt at the same temperature.

7(or 6)-Hydroxy-1-keto-6(or 7)-methoxy-2-methyltetrahydroisoquinoline (IV, p. 265).

Five grams of 1-keto-6:7-dimethoxy-2-methyltetrahydroisoquinoline and 30 c.c. of concentrated hydrochloric acid were heated together under pressure for two hours at 130—135°. The product consisted of a pale brown liquor containing a mass of cream-coloured needles, which formed the hydrochloride of the new base. The solid matter was collected, dissolved in a little hot water, and, after some time, 3.2 grams of the base separated in spear-like crystals, which melted at 200—208°, but contained some quantity of the dihydroxy-base, since they gave a green coloration with aqueous ferric chloride.

After recrystallisation from absolute alcohol, 7(or 6)-hydroxy-1-keto-6(or 7)-methoxy-2-methyltetrahydroisoquinoline forms colourless, glistening, diamond-shaped plates, which soften from 200°, melt at 210° (corr.), and give no coloration with aqueous ferric chloride:

0.1529 gave 0.3562 CO₂ and 0.0864 H₂O. C = 63.5; H = 6.3.

0.1555 „ 0.3635 CO₂ „ 0.0880 H₂O. C = 63.8; H = 6.3.

C₁₁H₁₃O₃N requires C = 63.8; H = 6.3 per cent.

This compound is very sparingly soluble in cold water, sparingly so in hot water or cold alcohol, readily so in hot alcohol, and sparingly or very sparingly so in the other usual organic solvents. It is insoluble in dilute acids, but soluble in aqueous sodium carbonate or ammonia, and dissolves readily in aqueous sodium hydroxide, forming a sodium salt which may be obtained as a crystalline mass by evaporating the solution to a very small bulk in a vacuum over sulphuric acid; this salt is very easily soluble in water or alcohol.

6:7-Dihydroxy-1-keto-2-methyltetrahydroisoquinoline (V, p. 265).

Ten grams of 1-keto-6:7-dimethoxy-2-methyltetrahydroisoquinoline and 60 c.c. of concentrated hydrochloric acid were heated together under pressure for three hours at 145—150°. The product consisted of a pale brown liquor containing pale brown needles; the latter were collected and digested successively with warm water and a little

boiling alcohol. The residue amounted to 3·4 grams of nearly pure dihydroxy-compound, and the alcohol deposited further small quantities of this compound. 6:7-Dihydroxy-1-keto-2-methyltetrahydroisoquinoline crystallises from absolute alcohol in beautiful colourless grains, which show a large number of sharply cut faces. It begins to sinter at about 250°, and melts at 279° (corr.):

0·1504 gave 0·3400 CO₂ and 0·0788 H₂O. C = 61·7; H = 5·9.

0·1555 „ 10·2 c.c. N₂ at 25° and 768 mm. N = 7·4.

C₁₆H₁₁O₃N requires C = 62·1; H = 5·8; N = 7·3 per cent.

This compound is sparingly soluble in boiling water or alcohol, and almost insoluble in these solvents when cold. It is insoluble in dilute acids, but easily soluble in aqueous ammonia, sodium carbonate, or sodium hydroxide, forming yellow solutions which gradually darken on exposure to air. Aqueous suspensions of this substance give, with ferric chloride solution, a faint green coloration, which gradually develops to deep green as the substance dissolves.

3:4-Dihydroxyphenylethylmethylamine (VII, p. 265).

Ten grams of 1-keto-6:7-dimethoxy-2-methyltetrahydroisoquinoline and 60 c.c. of concentrated hydrochloric acid were heated together under pressure for three hours at 170—175°.* The acid was then removed by distillation under diminished pressure, and the resulting slate-grey crystals of 3:4-dihydroxyphenylethylmethylamine hydrochloride were washed with acetone. The yield amounted to 8·5 grams, that is, 92 per cent. of the theoretical, and the crude product was purified by crystallisation from water containing sulphurous acid.

3:4-Dihydroxyphenylethylmethylamine is liberated in a crystalline form on the addition of ammonia to an aqueous solution of the hydrochloride. It crystallises from absolute alcohol in colourless clusters of transparent spikes, which melt at 188—189° (corr.). It is sparingly soluble in cold water, more easily so in hot water, sparingly so in boiling alcohol, and very sparingly so in cold alcohol and the usual organic solvents:

0·1524 gave 0·3611 CO₂ and 0·1090 H₂O. C = 64·6; H = 8·0.

0·1567 „ 11·0 c.c. N₂ at 17° and 778 mm. N = 8·3.

C₉H₁₃O₂N requires C = 64·6; H = 7·9; N = 8·4 per cent.

Aqueous solutions of the salts of this base give with ferric chloride solution a deep emerald-green coloration, which becomes orange-brown on the addition of aqueous sodium carbonate; such solutions reduce warm aqueous silver nitrate and boiling Fehling's solution; they give no precipitate with aqueous picric acid.

* On opening the tube, a large volume of gases containing a quantity of carbon dioxide escaped.

The *hydrochloride* crystallises from water in long, colourless prisms, which melt at $179-180^{\circ}$ (corr.). This salt is anhydrous, and is easily soluble in water or hot alcohol, but somewhat sparingly so in cold alcohol:

0.1505 gave 0.2944 CO_2 and 0.0939 H_2O . $\text{C} = 53.3$; $\text{H} = 7.0$.

0.1843 „ 0.1281 AgCl . $\text{Cl} = 17.2$.

$\text{C}_9\text{H}_{13}\text{O}_2\text{N} \cdot \text{HCl}$ requires $\text{C} = 53.1$; $\text{H} = 6.9$; $\text{Cl} = 17.4$ per cent.

The *sulphate* crystallises from water in colourless, transparent prisms, which melt to a brown liquid at $289-290^{\circ}$ (corr.), after commencing to soften and turn brown several degrees earlier. This salt is anhydrous, and is somewhat sparingly soluble in cold water:

0.1524 gave 0.2779 CO_2 and 0.0905 H_2O . $\text{C} = 49.7$; $\text{H} = 6.6$.

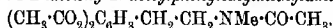
$(\text{C}_9\text{H}_{13}\text{O}_2\text{N})_2 \cdot \text{H}_2\text{SO}_4$ requires $\text{C} = 50.0$; $\text{H} = 6.5$ per cent.

The *oxalate* separates from water in colourless, hexagonal plates, which melt at $194-195^{\circ}$ (corr.). This salt is anhydrous, and is sparingly soluble in cold water:

0.1524 gave 0.3168 CO_2 and 0.0938 H_2O . $\text{C} = 56.7$; $\text{H} = 6.9$.

$(\text{C}_9\text{H}_{13}\text{O}_2\text{N})_2 \cdot \text{C}_2\text{H}_2\text{O}_4$ requires $\text{C} = 56.6$; $\text{H} = 6.7$ per cent.

3:4-Diacetoxy-N-acetylphenylethylmethylamine,



Two grams of 3:4-dihydroxyphenylethylmethylamine hydrochloride, 5 grams of fused sodium acetate, and 20 c.c. of acetic anhydride were boiled for half an hour under a reflux condenser. The product was stirred into 100 c.c. of water, the resulting clear solution rendered alkaline with sodium carbonate, and extracted with ether. On distilling the ether to low bulk and setting aside, 2.1 grams of the pure compound crystallised out, and a further small quantity was obtained from the mother liquor.

3:4-Diacetoxy-N-acetylphenylethylmethylamine crystallises from absolute alcohol in shimmering, hexagonal, monoclinic plates, which soften at 111° and melt at $113-114^{\circ}$ (corr.). It is very sparingly soluble in water or dilute acids, but dissolves slowly in dilute aqueous ammonia or sodium hydroxide, giving respectively greenish-yellow and strawberry-red solutions. It is sparingly soluble in cold alcohol or ether:

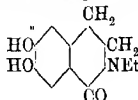
0.1728 gave 0.3895 CO_2 and 0.1006 H_2O . $\text{C} = 61.5$; $\text{H} = 6.5$.

0.1522 „ 6.1 c.c. N_2 at 21° and 775 mm. $\text{N} = 4.7$.

$\text{C}_{15}\text{H}_{19}\text{O}_5\text{N}$ requires $\text{C} = 61.4$; $\text{H} = 6.5$; $\text{N} = 4.8$ per cent.

Action of Hydrochloric Acid at 175° on 1-Keto-6:7-dimethoxy-2-ethyltetrahydroisoquinoline.

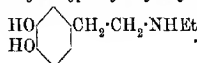
Four and a-half grams of 1-keto-6:7-dimethoxy-2-ethyltetrahydroisoquinoline and 30 c.c. of concentrated hydrochloric acid were heated together under pressure for three hours at 175°. The resulting clear brown liquor was evaporated to dryness under diminished pressure and dissolved in 15 c.c. of water, when 0.8 gram of 6:7-dihydroxy-1-keto-2-ethyltetrahydroisoquinoline separated in pale brown crystals; after removing these, the process was repeated, when a further quantity of 0.4 gram of the same product was obtained. The mother liquor gave on evaporation 3:4-dihydroxyphenylethylethylamine hydrochloride, of which 1.5 grams were obtained in a pure form by crystallisation from water.

6:7-Dihydroxy-1-keto-2-ethyltetrahydroisoquinoline,

This compound crystallises from absolute alcohol in beautifully crystalline rods, which begin to sinter at about 200°, and melt at 214—215° (corr.). Its chemical properties and solubilities are similar to those of the methyl homologue, with the exception of its solubility in absolute alcohol, which is greater:

0.1524 gave 0.3573 CO₂ and 0.0866 H₂O. C = 63.9; H = 6.4.

C₁₁H₁₃O₃N requires C = 63.8; H = 6.3 per cent.

3:4-Dihydroxyphenylethylethylamine,

The *hydrochloride* crystallises from water in prismatic needles, which melt at 177—178° (corr.). Its chemical properties and solubilities are similar to those of the methyl homologue, except that its aqueous solution does not yield a precipitate of the corresponding base on the addition of ammonia:

0.1519 gave 0.3057 CO₂ and 0.1024 H₂O. C = 55.0; H = 7.6.

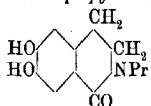
0.1819 „ 0.1239 AgCl. Cl = 16.8.

C₁₀H₁₅O₂N.HCl requires C = 55.1; H = 7.4; Cl = 16.3 per cent.

Action of Hydrochloric Acid at 175° on 1-Keto-6:7-dimethoxy-2-propyltetrahydroisoquinoline.

Two grams of 1-keto-6:7-dimethoxy-2-propyltetrahydroisoquinoline and 15 c.c. of concentrated hydrochloric acid, heated together under pressure for three hours at 175°, and worked up as in the preceding case, gave 1.4 grams of 6:7-dihydroxy-1-keto-2-propyltetrahydroisoquinoline and 0.4 gram of 3:4-dihydroxyphenylethylpropylamine hydrochloride.

6:7-Dihydroxy-1-keto-2-propyltetrahydroisoquinoline,

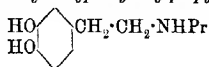


This compound separates from absolute alcohol in oblong, rectangular plates, which melt at 184—185° (corr.). Its chemical properties and solubilities are similar to those of the ethyl homologue:

0.1548 gave 0.3677 CO₂ and 0.0959 H₂O. C = 64.8; H = 6.9.

C₁₂H₁₅O₃N requires C = 65.1; H = 6.9 per cent.

3:4-Dihydroxyphenylethylpropylamine,



The *hydrochloride* crystallises from water in clusters of transparent, irregular prisms, which melt at 184—185° (corr.). Its chemical properties and solubilities are similar to those of the ethyl homologue:

0.1540 gave 0.3200 CO₂ and 0.1091 H₂O. C = 56.7; H = 7.9.

C₁₁H₁₇O₂N.HCl requires C = 57.0; H = 7.9 per cent.

6:7-Dihydroxy-2-methyltetrahydroisoquinoline (XIV, p. 268).

Eight and a-half grams of 6:7-dimethoxy-2-methyltetrahydroisoquinoline hydrochloride (containing 3 molecules of water of crystallisation) and 30 c.c. of concentrated hydrochloric acid were heated in a sealed tube for five hours at 170°. On cooling, 4.7 grams of 6:7-dihydroxy-2-methyltetrahydroisoquinoline hydrochloride separated in grey needles, that is, 76 per cent. of the theoretical.

6:7-Dihydroxy-2-methyltetrahydroisoquinoline separates on the addition of sodium carbonate to an aqueous solution of the hydrochloride. It crystallises from water in nearly colourless (pale buff)

needles, which melt at 221° — 222° (corr.), and contain one molecule of water of crystallisation. It is very sparingly soluble in water and the usual organic solvents.

Aqueous solutions of its salts give with ferric chloride a deep green coloration, which becomes mauve on the addition of sodium carbonate. They reduce hot silver nitrate and also boiling Fehling's solution:

0.1833 * lost 0.0172 at 100° . $H_2O = 9.4$.

0.1500 † gave 0.3693 CO_2 and 0.0987 H_2O . $C = 67.1$; $H = 7.4$.

$C_{10}H_{12}O_2N, H_2O$ requires $H_2O = 9.1$ per cent.

$C_{10}H_{13}O_2N$ requires $C = 67.0$; $H = 7.3$ per cent.

The hydrochloride crystallises from water in colourless needles, which are anhydrous and melt at 277° (corr.). It is fairly easily soluble in water, but sparingly so in alcohol:

0.1522 gave 0.3093 CO_2 and 0.0937 H_2O . $C = 55.4$; $H = 6.9$.

0.1721 „ 0.1144 $AgCl$. $Cl = 16.4$.

$C_{10}H_{13}O_2N, HCl$ requires $C = 55.7$; $H = 6.6$; $Cl = 16.4$ per cent.

The picrate crystallises from alcohol in transparent, yellow, monoclinic hexagonal plates, which melt at 191° — 192° (corr.).

Phenobetaine of 6:7-Dihydroxy-2-methyl-3:4-dihydroisoquinolinium Hydroxide (XVI or XVII, p. 268).

Ten grams of 6:7-dimethoxy-2-methyl-3:4-dihydroisoquinolinium chloride and 60 c.c. of concentrated hydrochloric acid were heated together under pressure for four hours at 170° . The product was evaporated to dryness under diminished pressure, and the crystalline residue well washed with acetone. 6.5 Grams of nearly pure anhydrous 6:7-dihydroxy-2-methyl-3:4-dihydroisoquinolinium chloride were obtained, the yield thus amounting to 93 per cent. of the theoretical.

The phenobetaine of 6:7-dihydroxy-2-methyl-3:4-dihydroisoquinolinium hydroxide separates in long, deep yellow needles containing one and a-quarter molecular proportions of water of crystallisation on the addition of the calculated quantity of aqueous sodium hydroxide, or an excess of sodium carbonate to a strong solution of its chloride:

0.1816 * lost 0.0201 at 100° . $H_2O = 11.1$.

$C_{10}H_{11}O_2N, 1\frac{1}{4}H_2O$ requires $H_2O = 11.3$ per cent.

After recrystallisation from moist alcohol it forms deep yellow, monoclinic plates, which melt to a reddish-black liquid, decompose at 222° (corr.), and contain 1 molecule of water of crystallisation:

0.1543 * gave 0.2667 CO_2 and 0.0746 H_2O . $C = 61.5$; $H = 7.0$.

* Air-dried.

† Dried at 100° .

0.1380 * gave 0.3096 CO_2 and 0.0839 H_2O . $\text{C} = 61.2$; $\text{H} = 6.8$.

$\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}\cdot\text{H}_2\text{O}$ requires $\text{C} = 61.5$; $\text{H} = 6.8$ per cent.

0.1388 † gave 0.3448 CO_2 and 0.0795 H_2O . $\text{C} = 67.7$; $\text{H} = 6.4$.

$\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}$ requires $\text{C} = 67.8$; $\text{H} = 6.3$ per cent.

The phenolbetaine crystallises from absolute alcohol in anhydrous, yellowish-brown, serrated spikes, which have the same melting point as the hydrated base, is moderately easily soluble in cold water, not more so in aqueous sodium carbonate or ammonia, but readily in dilute acids or aqueous sodium hydroxide. It is rather sparingly soluble in cold alcohol or chloroform, and very sparingly so in the other usual organic solvents. Aqueous solutions of its salts give with aqueous ferric chloride a deep green coloration, and on the subsequent addition of sodium carbonate yield a pale reddish-brown suspension, the supernatant liquor appearing a dull yellow after the settlement of the ferric hydroxide. Aqueous solutions of the salts of this base reduce hot silver nitrate, but do not reduce Fehling's solution even on boiling.

The chloride crystallises from moist acetone in primrose needles, which contain one and a-half molecular proportions of water of crystallisation. After drying at 100° , this salt melts and decomposes; at 276° (corr.). It is easily soluble in water, but sparingly so in alcohol:

0.4060, air-dried salt, lost 0.0437 at 100° . $\text{H}_2\text{O} = 10.8$.

$\text{C}_{10}\text{H}_{12}\text{O}_2\text{NCl}\cdot\frac{1}{2}\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 11.2$ per cent.

0.1468 † gave 0.3019 CO_2 and 0.0743 H_2O . $\text{C} = 56.1$; $\text{H} = 5.7$.

0.1593 † „ 0.1081 AgCl . $\text{Cl} = 16.8$.

$\text{C}_{10}\text{H}_{12}\text{O}_2\text{NCl}$ requires $\text{C} = 56.2$; $\text{H} = 5.7$; $\text{Cl} = 16.6$ per cent.

The picrate crystallises from alcohol in yellow, transparent, irregular plates, which melt and decompose at 236° (corr.).

The sodium salt separates in clusters of beautiful crimson needles on the addition of alcohol to a solution of the phenolbetaine in the calculated quantity of 2*N*-aqueous sodium hydroxide. It is easily soluble in water or alcohol. This salt contains 6 molecules of water of crystallisation, of which five are lost after prolonged heating at 120° :

0.2530 * gave 0.0562 Na_2SO_4 . $\text{Na} = 7.2$.

0.2541 * lost 0.0763 at 120° . $\text{H}_2\text{O} = 30.0$.

$\text{C}_{10}\text{H}_{10}\text{O}_2\text{NNa}\cdot 6\text{H}_2\text{O}$ requires $\text{Na} = 7.5$; loss of $5\text{H}_2\text{O} = 29.3$ per cent.

Action of Methyl Iodide on the Phenolbetaine of 6:7-Dihydroxy-2-methyl-3:4-dihydroisoquinolinium Hydroxide.

Eight grams of the phenolbetaine, which had been dried for some time at 100° , were heated together with 16 grams of methyl iodide for

* Air-dried.

† Dried at 100° .

three hours at 100°. The crystalline product obtained was separated by fractional crystallisation from absolute alcohol into:

(1) 7.2 grams of 7(or 6)-hydroxy-6(or 7)-methoxy-2-methyl-3 : 4-dihydroisoquinolinium iodide, melting at 213° (corr.).

(2) 2.0 grams of 6(or 7)-methoxy-7(or 6)-[6 : 7-dihydroxy-2-methyl-3 : 4-dihydroisoquinolinumoxy]-2-methyl-3 : 4-hydroisoquinolinium iodide, melting at 181—182° (corr.), and

(3) a small quantity of a brown, gummy residue.

In a second experiment, in which the phenolbetaine was not previously dried at 100°, a larger proportion of the latter compound was obtained, 11 grams of hydrated phenolbetaine and 25 grams of methyl iodide yielding 4.4 grams of the first-mentioned iodide and 5.1 grams of the latter, besides an oily residue which was neglected.

7(or 6)-Hydroxy-6(or 7)-methoxy-2-methyl-3 : 4-dihydroisoquinolinium Salts (XVIII, p. 269).

The *iodide* crystallises from alcohol in fine long, golden needles, which melt and decompose at 218° (corr.). It is anhydrous, and is sparingly soluble in water or alcohol :

0.1536 gave 0.2336 CO₂ and 0.0611 H₂O. C = 41.5; H = 4.5.

0.1876 „ 0.1370 AgI. I = 39.5.

0.3046 „ by Zeisel's method 0.2098 AgI. OMe = 9.1.

C₁₁H₁₄O₂NI requires C = 41.4; H = 4.4; I = 39.8; OMe = 9.7 per cent.

The *chloride* was obtained from the iodide by double decomposition with silver chloride. It crystallises from aqueous acetone in yellow needles, which contain one molecule of water of crystallisation, and effervesce at 155° (corr.), after sintering from about 140°; after drying at 100°, it decomposes at 198° (corr.). It is easily soluble in water or hot alcohol, and its aqueous solution gives no coloration with ferric chloride solution :

0.2011 * lost 0.0146 at 100°. H₂O = 7.3.

C₁₁H₁₄O₂NCl.H₂O requires H₂O = 7.3 per cent.

0.1400 † gave 0.2970 CO₂ and 0.0815 H₂O. C = 57.9; H = 6.5.

0.1818 † „ 0.1134 AgCl. Cl = 15.4

C₁₁H₁₄O₂NCl requires C = 58.0; H = 6.2; Cl = 15.6 per cent.

On dissolving this salt in warm concentrated aqueous ammonia, a deep red solution is obtained, which deposits, on cooling, orange crystals of the chloride of the external phenolbetaine, namely, 6(or 7)-methoxy-7(or 6)-[7(or 6)-hydroxy-6(or 7)-methoxy-2-methyl-3 : 4-dihydroisoquinolinumoxy]-2-methyl-3 : 4-dihydroisoquinolinium chloride (XX, p. 269).

After recrystallisation from absolute alcohol, this salt forms bright

* Air-dried.

† Dried at 100°.

orange prisms, which contain $3\frac{1}{2}\text{H}_2\text{O}$ and melt and decompose at 135° (corr.). It is easily soluble in water, but sparingly so in cold absolute alcohol; it contains chlorine. On heating this salt at 100° , it first becomes crimson, and then melts to a deep red gum which retains about 1 per cent. of water of crystallisation:

0.1413 * gave 0.2831 CO_2 and 0.0933 H_2O . $\text{C} = 54.6$; $\text{H} = 7.3$.

0.1193 * lost 0.0146 at 100° . $\text{H}_2\text{O} = 12.2$.

$\text{C}_{25}\text{H}_{27}\text{O}_4\text{N}_2\text{Cl}, 3\frac{1}{2}\text{H}_2\text{O}$ requires $\text{C} = 54.8$; $\text{H} = 7.1$; $\text{H}_2\text{O} = 13.1$ per cent.

0.1047 † gave 0.2397 CO_2 and 0.0624 H_2O . $\text{C} = 63.4$; $\text{H} = 6.6$.

$\text{C}_{22}\text{H}_{27}\text{O}_4\text{N}_2\text{Cl}$ requires $\text{C} = 63.1$; $\text{H} = 6.5$ per cent.

6(or 7)-Methoxy-7(or 6)-[6:7-dihydroxy-2-methyl-3:4-dihydroisoquinoliniumoxy]-2-methyl-3:4-dihydroisoquinolinium Salts (XIX, p. 269).

The iodide crystallises from absolute alcohol in hard, orange grains, which melt and decompose at $181\text{--}182^\circ$ (corr.). It is anhydrous and easily soluble in water, but sparingly so in cold alcohol. Its aqueous solution gives a deep green coloration with ferric chloride solution:

0.1524 gave 0.2826 CO_2 and 0.0713 H_2O . $\text{C} = 50.6$; $\text{H} = 5.2$.

0.1867 " 0.0896 AgI . $\text{I} = 25.9$.

$\text{C}_{21}\text{H}_{25}\text{O}_4\text{N}_2\text{I}$ requires $\text{C} = 50.8$; $\text{H} = 5.1$; $\text{I} = 25.6$ per cent.

On adding a molecular proportion of hydriodic acid to the deep orange aqueous solution of 2 grams of this salt, a pale yellow solution was obtained. On evaporating this to low bulk and adding absolute alcohol, 0.9 gram of 7(or 6)-hydroxy-6(or 7)-methoxy-2-methyl-3:4-dihydroisoquinolinium iodide separated; after recrystallisation, this melted at 218° (corr.), both alone and when mixed with the pure salt, and gave no coloration with aqueous ferric chloride. On then adding ammonia to the mother liquor, a small quantity of the phenolbetaine of 6:7-dihydroxy-2-methyl-3:4-dihydroisoquinolinium hydroxide separated; after recrystallisation from alcohol, this compound melted at 222° (corr.), and its melting point suffered no depression when the compound was mixed with the pure phenolbetaine.

The chloride was prepared from the iodide by double decomposition with silver chloride. It crystallises from absolute alcohol in deep yellow, glistening prisms, which melt at $186\text{--}187^\circ$ (corr.), and contain one molecule of water of crystallisation:

0.3360 * lost 0.0169 at 100° . $\text{H}_2\text{O} = 5.0$.

$\text{C}_{21}\text{H}_{25}\text{O}_4\text{N}_2\text{Cl}, \text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 4.3$ per cent.

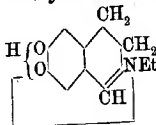
0.1416 † gave 0.3251 CO_2 and 0.0810 H_2O . $\text{C} = 62.6$; $\text{H} = 6.4$.

$\text{C}_{21}\text{H}_{25}\text{O}_4\text{N}_2\text{Cl}$ requires $\text{C} = 62.3$; $\text{H} = 6.2$ per cent.

* Air-dried.

† Dried at 100° .

Phenolbetaine of 6 : 7-dihydroxy-2-ethyl-3 : 4-dihydroisoquinolinium Hydroxide,



The preparation and properties of this compound and its salts are similar to those of the corresponding methyl-homologue.

The *phenolbetaine of 6 : 7-dihydroxy-2-ethyl-3 : 4-dihydroisoquinolinium hydroxide* crystallises from absolute alcohol in deep yellow rods, which melt and decompose at 235° (corr.). It is anhydrous:

0.1443 gave 0.3661 CO_2 and 0.0919 H_2O . $\text{C} = 69.2$; $\text{H} = 7.1$.

$\text{C}_{11}\text{H}_{18}\text{O}_2\text{N}$ requires $\text{C} = 69.1$; $\text{H} = 6.9$ per cent.

The *chloride* crystallises from water in fine yellow needles, which melt at 104° (corr), and contain 2 molecules of water of crystallisation. After drying at 100° , this salt melts and decomposes at $201-202^{\circ}$ (corr.):

0.2170 * lost 0.0300 at 100° . $\text{H}_2\text{O} = 13.8$.

$\text{C}_{11}\text{H}_{14}\text{O}_2\text{NCl} \cdot 2\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 13.7$ per cent.

0.1517 † gave 0.3221 CO_2 and 0.0845 H_2O . $\text{C} = 58.0$; $\text{H} = 6.2$.

0.1475 † „ 0.0943 AgCl . $\text{Cl} = 15.8$.

$\text{C}_{11}\text{H}_{14}\text{O}_2\text{NCl}$ requires $\text{C} = 58.0$; $\text{H} = 6.2$; $\text{Cl} = 15.6$ per cent.

The *picrate* crystallises from alcohol in clusters of golden, spear-like needles, which melt and decompose at 191° (corr.).

THE WELLCOME CHEMICAL WORKS
DARTFORD, KENT.

XXIX.—The Absorption Spectra of Naphthalene and of Tetramethylnaphthalene.

By ANNIE HOMER and JOHN EDWARD PURVIS.

IN a paper on the absorption spectra of the hydrocarbons isolated from the products of the action of aluminium chloride on naphthalene (Homer and Purvis, *Trans.*, 1908, 93, 1319), we described the absorption spectrum of a substance having the empirical formula $\text{C}_{14}\text{H}_{10}$. From chemical considerations it had been suggested that

Air-dried.

† Dried at 100° .

this hydrocarbon was an alkyl, probably a tetramethyl, derivative of naphthalene, and it was thought that a comparison of the absorption spectrum of this hydrocarbon with that of naphthalene would furnish additional evidence as to its constitution.

Hartley, in his earlier work (Trans., 1881, 29, 153), showed that the absorption spectrum of naphthalene was characterised by four bands in the ultraviolet region of the spectrum. In a later paper, Hartley (Trans., 1885, 47, 685) showed that there were four bands, the positions of which differed from those of the earlier observations. The method employed by Hartley differed from that used by us, and described in the previous paper (*loc. cit.*). For purposes of comparison it was necessary for us to study the absorption spectrum of naphthalene under the same experimental conditions as those employed in the study of the hydrocarbons under investigation. Our results showed that for $N/1000$ -solutions in alcohol, the absorption curve for naphthalene, as observed by Hartley in his first paper, showed four characteristic bands. The mean oscillation frequencies of these bands did not coincide with those given by Hartley, but we did not comment on the discrepancies at the time of our previous work. The curve for $N/1000$ -solutions of the hydrocarbon $C_{14}H_{16}$ also showed four bands, similar in character to the naphthalene bands, although less persistent and further shifted towards the red end of the spectrum (Fig. 1).

The mean oscillation frequencies of the bands were :

For naphthalene, Hartley, first paper	3508	3690	3840	3921
" " second paper ...	3211	3273	3369	3849
" Homer and Purvis (not previously published)..	3500	3620	3765	3900
For $C_{14}H_{16}$, Homer and Purvis	3434	3562	3680	3776

From these results we concluded that the substance $C_{14}H_{16}$ was probably tetramethylnaphthalene, as had been previously suggested (Homer, Trans., 1907, 91, 1103).

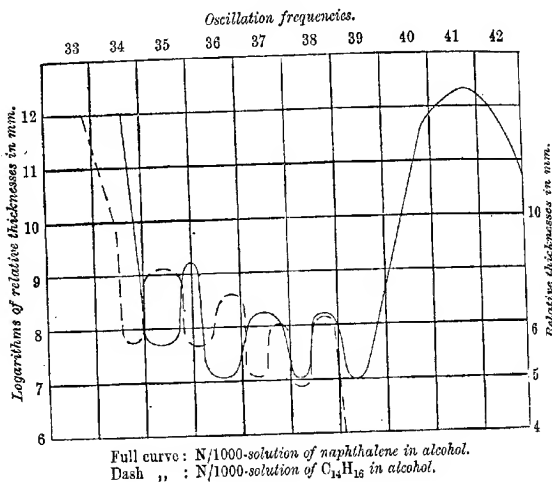
Since the publication of these results, Baly and Tuck (Trans., 1908, 93, 1902), in their work on the absorption spectra of aromatic hydrocarbons, have shown that for naphthalene there are three characteristic bands having mean oscillation frequencies : $1/\lambda = 3125$, $1/\lambda = 3220$, and $1/\lambda = 3700$. The bands $1/\lambda = 3125$ and $1/\lambda = 3220$ only appear in strong solutions or in proportionately greater thicknesses of dilute solutions. The band $1/\lambda = 3700$ is a broad band, and corresponds with the four bands observed by Hartley in his first paper (Trans., 1881, 39, 153) and also by us.

After reading Baly and Tuck's paper, it seemed necessary for us to re-examine the absorption spectrum of the hydrocarbon $C_{14}H_{16}$. For if, as we had previously surmised, the hydrocarbon $C_{14}H_{16}$ is a tetra-

methyl derivative of naphthalene, there should be indications of bands corresponding with the naphthalene bands, $1/\lambda$ 3125 and $1/\lambda$ 3220, observed by Baly and Tuck. The absence of such bands would, according to these observers, point to a difference between the constitution of naphthalene and of the hydrocarbon $C_{14}H_{16}$.

At the time of our previous experiments we had only sufficient of the hydrocarbon with which to make a $N/1000$ -solution. This strength was compared with a similar $N/1000$ -solution of naphthalene. These solutions gave the four bands already described, and corresponding with the broad band, $1/\lambda$ 3700, of Baly and Tuck. Since then the

FIG. 1.



hydrocarbon has been made in larger quantity, and we have been able to compare its $N/10$ -solution with a similar solution of naphthalene. The results have been plotted in the accompanying curves (Fig. 2).

It will be seen from a glance at the curves, that for $N/10$ -solution of naphthalene there are two bands similar to those obtained by Baly and Tuck. The curve for the hydrocarbon $C_{14}H_{16}$ also shows two similar bands, less persistent and further shifted towards the red end of the spectrum than the naphthalene bands.

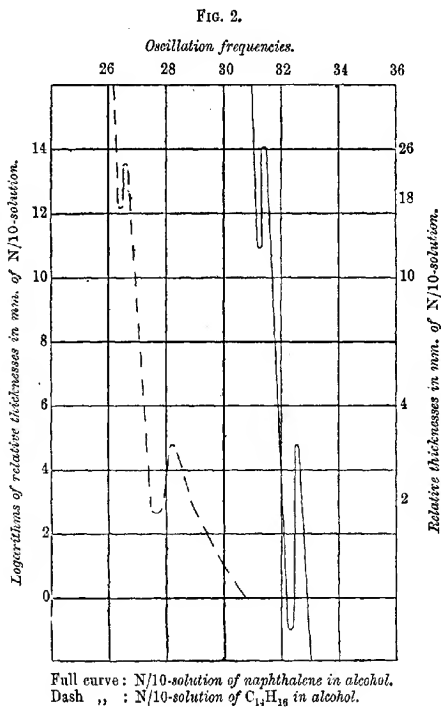
The mean oscillation frequencies of the bands are:

Naphthalene, Baly and Tuck	3125	3220
$N/10$ -solution, Homer and Purvis ...	3122	3225
$C_{14}H_{16}$, $N/10$ -solution, " " " ...	2638	2770

The results of our investigation may be summarised as follows:

I. The absorption curves for both $N/1000$ - and $N/10$ -solutions of the hydrocarbon $C_{14}H_{10}$ are similar to the curves for naphthalene. These results are in accordance with our previous suggestion that the substance is a tetramethyl derivative of naphthalene.

II. Our experiments confirm the observation of Baly and Tuck



with regard to the presence of bands corresponding with $1/\lambda$ 3125 and $1/\lambda$ 3220 in naphthalene and its derivative.

III. Hartley in his first paper represented the naphthalene curve for dilute solutions as being characterised by the presence of four narrow bands. Baly and Tuck from their results consider that there is only one broad band, $1/\lambda$ 3700, which corresponds with Hartley's

four bands. The curves obtained by us for 1/1000-solutions of naphthalene, and of its derivative, $C_{14}H_{10}$, shows four narrow bands. These observations support Hartley's first interpretation of the absorption curve of naphthalene.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

XXX.—*The Alkaloids of Ergot. Part II.*

By GEORGE BARGER and ARTHUR JAMES EWINS.

In a previous communication on this subject (Trans., 1907, 91, 337), one of us, in conjunction with F. H. Carr, described the new amorphous alkaloid ergotoxine, $C_{35}H_{41}O_6N_5$, and assigned to Tanret's crystalline ergotinine the formula $C_{35}H_{39}O_6N_5$. The crystalline alkaloid was thus proved to be the anhydride of the amorphous one, as was first surmised by Kraft.¹

The transformation of ergotoxine into ergotinine takes place by boiling with methyl alcohol (Kraft), or with acetic anhydride. When, on the other hand, ergotinine was warmed on the water-bath with very dilute phosphoric acid, Barger and Carr obtained from it the crystalline phosphate of an amorphous base, which closely resembled ergotoxine phosphate in physiological action and had the same melting point; the crystalline form was, however, entirely different. Ergotoxine phosphate crystallises in thin needles (Fig. 2), the new phosphate formed rhomb-shaped, triangular, or hexagonal plates (Fig. 1), and the difference persisted after the bases had been liberated, dissolved in ether, and again converted into their phosphates by precipitation with alcoholic phosphoric acid.

We have now found the cause of this difference between the two salts. When ergotinine is heated with a solution of phosphoric acid in ethyl alcohol, there is formed, not ergotoxine phosphate, but the phosphate of ergotoxine ethyl ester, and it is the latter salt which crystallises in plates. The hydrochlorides of the two bases are also quite different (Figs. 3 and 4). That the new base

* The identity of Kraft's hydroergotinine (*Arch. Pharm.*, 1906, 244, 336) with ergotoxine was recently doubted by Vahlen (*Arch. exp. Path. Pharm.*, 1908, 60, 42) on physiological grounds, but an analysis of hydroergotinine sulphate by Kraft (*Arch. Pharm.*, 1907, 245, 644) and a comparative physiological examination by Dale (*Arch. exp. Path. Pharm.*, 1909, 61, 113) leave no doubt that hydroergotinine and ergotoxine are synonymous terms.

is an ethyl ester was shown by analysis, and especially by a determination of the ethoxy-group by Zeisel's method.

It thus follows that ergotoxine contains a carboxyl group, and that ergotinine is its lactone (or lactam). In accordance with this view, ergotoxine is soluble in sodium hydroxide, but ergotinine is not, nor is the ester-base above referred to. Esterification probably takes place to some extent when ergotoxine is boiled with alcohol (in the absence of phosphoric acid). We have noticed repeatedly in converting ergotoxine into ergotinine by boiling with methyl alcohol (Kraft's method) that the yield is far from quantitative; some of the ergotoxine is probably converted by this process into the very soluble ethyl ester, instead of the crystalline anhydride. It is, moreover, quite likely that ergotinine itself when boiled with alcohol forms ergotoxine ester to some extent; this behaviour would explain the loss of ergotoxine on recrystallisation which we ourselves and others (Tauret, Meulenhoff) have noticed. The fall in optical rotation shown by alcoholic ergotinine solutions, especially on boiling, is also probably due to the formation of an ergotoxine ester.

Besides proving the presence of a carboxyl group in ergotoxine, we have been able to establish the presence of a somewhat larger, and more characteristic fragment of the complicated molecule of the ergot alkaloids. On destructive distillation, both ergotoxine and ergotinine yield a small quantity of a crystalline substance, and this we have been able to identify as isobutyrylformamide, $\text{CHMe}_2\text{CO}\cdot\text{CO}\cdot\text{NH}_2$. The yield of this substance is only 5 per cent. of the (very costly) alkaloid employed; as we had only a few decigrams of the substance at our disposal, its identification was somewhat troublesome, but was finally rendered certain by direct comparison with a specimen of isobutyrylformamide synthesised for the purpose.

A ketonic amide of this type does not appear to have been previously obtained from a natural substance, and we are unable to suggest the mechanism of its formation from the ergot alkaloids. We do not think, however, that either of the oxygen atoms of the amide belongs to the carboxyl group which we have shown to be present in ergotoxine. If this be admitted, we have accounted for four out of the six oxygen atoms of that alkaloid (or three out of the five present in ergotinine). The two remaining oxygen atoms are not present as phenolic hydroxy- or methoxy-groups, because ergotinine is insoluble in sodium hydroxide, and when examined by Zeisel's method yields a negative result. One of the nitrogen atoms probably has a methyl group attached to it, because some-

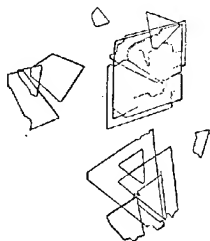
thing like one equivalent of methyl iodide is set free when ergotinine is examined by Herzig and Meyer's method. At least one of the five nitrogen atoms is tertiary, for a methiodide is slowly formed. It is remarkable that, in spite of having five nitrogen atoms, the ergot alkaloids are only very feeble mono-acid bases.

EXPERIMENTAL.

Phosphate of Ergotoxine Ethyl Ester, $C_{34}H_{40}O_4N_5 \cdot CO_2 \cdot C_2H_5 \cdot H_3PO_4$.

One gram of crystalline ergotinine was suspended in 10 c.c. of absolute ethyl alcohol; and 1.1 equivalent of phosphoric acid dissolved in 5 c.c. of alcohol was added. On warming on the water-bath for fifteen to thirty minutes, the ergotinine gradually dissolved; on cooling, an amorphous solid separated, which was collected and crystallised from 90—95 per cent. ethyl alcohol. In this way about 0.3 gram of a grey product was obtained, which

FIG. 1.



Phosphate of ergotoxine ethyl ester.
× 65 diameters.

FIG. 2.



Ergotoxine phosphate.
× 65 diameters.

on recrystallisation from 12 c.c. of 95 per cent. alcohol separated in almost white leaflets (Fig. 2), melting at 187—188° (bath previously heated to 180°). For the sake of comparison the crystalline form of ergotoxine phosphate is shown in Fig. 2. These and the other figures were drawn from micro-photographs:

0.1353 gave 0.2922 CO_2 and 0.0812 H_2O . $C = 58.9$; $H = 6.4$.

$C_{37}H_{45}O_6N_5 \cdot H_3PO_4$ requires $C = 58.9$; $H = 6.4$ per cent.

$C_{38}H_{41}O_6N_5 \cdot H_3PO_4$ " $C = 57.9$; $H = 6.1$ "

As the phosphate of an ethyl ester of ergotoxine contains only 1 per cent. more carbon than that of the corresponding ergotoxine salt, a direct determination of the ethoxy-group was made by Zeisel's method:

0.3503 gave 0.1064 AgI. $OEt = 5.82$.

$C_{34}H_{40}O_4N_2 \cdot CO_2Et \cdot H_3PO_4$ requires $OEt = 5.97$ per cent.

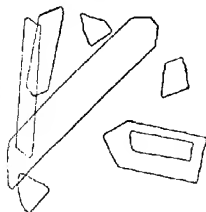
The rotation of this salt was also determined in 75 per cent. alcohol. $l = 1$ decm.; $c = 2.03$; $\alpha_D + 1.58^\circ$; $[\alpha]_D + 77.8^\circ$. From the phosphate obtained in the manner described, the base was set free by sodium carbonate, dissolved in ether, and dried with sodium sulphate. From the ethereal solution of the base obtained in this way, the hydrochloride and the oxalate were precipitated by adding alcoholic hydrochloric acid and ethereal oxalic acid solutions respectively.

Hydrochloride of Ergotoxine Ethyl Ester, $C_{37}H_{45}O_6N_2 \cdot HCl$.

The precipitated salt crystallised from 90 per cent. alcohol in large plates (Fig. 3), which melted at $206-207^\circ$ (bath previously heated to 190°). For the sake of comparison, crystals of ergotoxine hydrochloride (m. p. 205°) are shown in Fig. 4.*

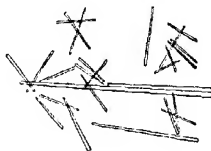
The difference in crystalline form existing between salts of ergotoxine and the corresponding salts of the ethyl ester is also clearly shown in the case of the oxalates formed by adding an

FIG. 3.



Hydrochloride of ergotoxine ethyl ester.
x 65 diameters.

FIG. 4.



Ergotoxine hydrochloride.
x 65 diameters.

ethereal solution of oxalic acid to the bases dissolved in ether. Both salts melt at $179-180^\circ$, but whereas the ergotoxine oxalate forms elongated, rectangular prisms, the salt of the ester crystallises in hexagonal leaflets.

By warming ergotinine with a solution of phosphoric acid in methyl alcohol, crystalline salts of ergotoxine methyl ester are readily obtainable. As in the case of the ethyl ester, this base is

* In the previous paper (Trans., 1907, 81, 350) it was stated that ergotoxine hydrochloride forms "diamond-shaped plates and very thin and very long, square-ended needles." The plates, however, were an admixture of the hydrochloride of ergotoxine ethyl ester.

amorphous, thus resembling ergotoxine; the ester bases differ, however, from ergotoxine in being insoluble in dilute sodium hydroxide.

Salts of Ergotoxine.

In addition to the phosphate, the hydrochloride, and the two oxalates of ergotoxine, which were described in the earlier paper, several other salts have been obtained crystalline. They were prepared in each case by adding a dilute ethereal or alcoholic solution of the acid to a solution of ergotoxine in ether, until no further precipitate was formed. The precipitated salt was dried in a vacuum, and crystallised from warm 90 to 95 per cent. alcohol. Not infrequently the salt separates as a jelly on cooling; in such cases it is best to dilute the solution, so that nothing separates on cooling, and then to add a few drops of dry ether at intervals.

Ergotoxine picrate forms pale yellow, acicular prisms, melting at 214–215° (bath first heated to 210°):

0.1536 gave 17.2 c.c. N_2 (moist) at 10.5° and 757 mm. $N=13.2$.

$C_{35}H_{41}O_6N_5 \cdot C_6H_3O_7N_3$ requires $N=13.1$ per cent.

Ergotoxine hydrobromide, acicular prisms, melting at 208°:

0.1042 gave 0.0260 AgBr. $Br=10.6$.

$C_{35}H_{41}O_6N_5 \cdot HBr$ requires $Br=11.3$ per cent.

Ergotoxine sulphate, prisms, melting at 197°:

0.1192 gave 0.0358 $BaSO_4$. $H_2SO_4=12.6$.

$C_{35}H_{41}O_6N_5 \cdot H_2SO_4$ requires $H_2SO_4=13.5$ per cent.

This appears to be a somewhat impure acid sulphate; that prepared by Kraft was the normal one.

Ergotoxine nitrate forms short, broad prisms, melting at 193–194°.

Action of Methyl Iodide on Ergotinine, Ergotoxine, and Ergotoxine Esters.

Ergotinine and allied bases appear to have one tertiary nitrogen atom. Ergotinine dissolves readily in methyl iodide, but when the solution is left at the laboratory temperature for some days, it is gradually transformed into a white jelly, readily soluble in alcohol; this jelly doubtless represents the methiodide. Ergotoxine and its esters behave in a similar way, except that the reaction is more rapid. In no case, however, could a crystalline product be isolated. We give as an example the analysis of the precipitate formed in a solution of ergotoxine methyl ester in methyl iodide; the substance, presumably the methiodide, was washed with dry ether and dried at 100°:

0.1300 gave 0.0385 AgI. $I=15.2$.

$C_{36}H_{42}O_6N_2CH_3I$ requires $I=16.2$ per cent.

Action of Absolute Alcohol on Ergotinine.

A solution of 0.24 gram of crystalline ergotinine in 100 c.c. of absolute ethyl alcohol was divided into two portions. A 2.2-dcm. polarimeter tube was filled with one portion of the solution, and kept in the dark at the laboratory temperature for some months. During this time the rotation gradually decreased, as shown by the following table:

	α_D	l	$[\alpha]_D$
June 11th	+1.76°	2.2 dcm.	+333°
June 12th	+1.71	2.2 "	+324
June 14th	+1.66	2.2 "	+314
June 17th	+1.61	2.2 "	+305
June 28th	+1.61	2.2 "	+305
July 19th	+1.52	2.2 "	+290
Sept. 13th	+0.62	1 "	+258

The other portion was heated under a reflux condenser on the water-bath; here the change was more rapid:

Time in hours.	α_D	l	$[\alpha]_D$
0	+1.76°	2.2 dcm.	+333°
1	+1.59	2 "	+331
4	+1.41	2 "	+294
8½	+0.67	2 "	+275
15½	+0.61	1 "	+254
23	+0.59	1 "	+246
30	+0.48	1 "	+200
37	+0.37	1 "	+154

In boiling alcoholic solution the change is even more rapid. A saturated solution prepared by shaking at 10° gave:

$l=2.2$ dcm.; $c=0.2566$; $\alpha_D+1.91^\circ$; $[\alpha]_D+338^\circ$.

After boiling for five minutes, $[\alpha]_D$ fell to 327°, after one hour to 300°, after three hours to 242°.

Crystals of ergotinine, obtained by rapidly cooling a boiling alcoholic solution, are shown below:

FIG. 5.



Ergotinine. $\times 65$ diameters.

Isolation of isoButyrylformamide on Destructive Distillation of the Ergot Alkaloids.

The formation of a crystalline sublimate can be observed by carefully heating a few milligrams of ergotinine or ergotoxine in a small tube. The alkaloids melt and decompose, and a minute quantity of a colourless liquid appears in the cold part of the tube; this soon crystallises, and if the operation is carried out under diminished pressure the substance appears at once in glistening leaflets.

It was soon found that the substance, once set free, sublimes at 100° , and cannot be recrystallised from organic solvents without great loss. Its purification was therefore carried out by sublimation under diminished pressure.

Ergotinine (in some cases ergotoxine) was heated in quantities of 0.5 gram at a time in a flask of 5–10 c.c. capacity, which was provided with a neck 25 cm. long and 1 cm. wide. Almost the whole of the bulb could be immersed in a metal-bath at 220 – 240° ; the lower part of the neck, adjoining the bulb, was jacketed with steam, and the flask was evacuated to 2 mm. pressure. By this means the crystalline sublimate collected only on the upper part of the neck, above the steam-jacket. It was contaminated with a little yellow oil, and was purified as follows. The region of the tube where the sublimate had condensed was cut off, placed in a test-tube, and the substance re-sublimed in a boiling water-bath under a pressure of 15 to 20 mm.; it condensed on the upper portion of the test-tube, from which it was removed by means of a glass rod. In this way 0.09 gram of pure sublimate was obtained from the base from 3 grams of somewhat impure ergotoxine phosphate; in another experiment, 0.5 gram of pure ergotinine yielded 0.021 gram of sublimate, or 4.2 per cent.

As thus obtained, the substance formed thin, large, glistening leaflets, melting in a sealed tube at 109° , readily soluble in cold alcohol, but only sparingly so in cold water and in benzene:

0.0467 gave 0.0881 CO_2 and 0.0325 H_2O . $\text{C}=51.1$; $\text{H}=7.4$.

0.1034 „ 0.1946 CO_2 „ 0.0756 H_2O . $\text{C}=51.3$; $\text{H}=8.1$.

0.0860 „ 8.8 c.c. N_2 (moist) at 19° and 767 mm. $\text{N}=12.0$.

$\text{C}_8\text{H}_9\text{O}_2\text{N}$ requires $\text{C}=52.1$; $\text{H}=7.8$; $\text{N}=12.2$ per cent.

The vapour-density was determined by Victor Meyer's method:

0.0913 gave 22.05 c.c. moist air at 17° and 762 mm. $\text{V.D.}=53$.

$\text{C}_8\text{H}_9\text{O}_2\text{N}=115$ requires $\text{V.D.}=57.5$.

Although the percentage of carbon found is rather low, the formula $\text{C}_8\text{H}_9\text{O}_2\text{N}$ is established with certainty. At first we found

several per cent. too much nitrogen, until we employed cuprous chloride (compare Haas, Trans., 1906, 89, 570). The same difficulty was experienced by Barger and Carr in determining the nitrogen in ergotinine (Trans., 1907, 91, 343, footnote), and is apparently due to the presence of a *gem*-dimethyl group, resulting in the formation of methane. We have now actually located this dimethyl group in isobutyrylformamide, where, on analysis by Dumas's method, unless cuprous chloride or lead chromate is used, it produces a much larger error than when accompanied by the rest of the molecule in ergotinine. Some of this methane probably also escaped combustion in the carbon and hydrogen estimations quoted.

The melting point of our substance corresponded closely with three substances of the formula $C_5H_9O_2N$ described in the literature, namely, butyrylformamide, isobutyrylformamide, and levulinamide.

We first prepared butyrylformamide by the method given below. This substance was found to have a striking resemblance to the sublimate from the ergot alkaloids, and melted at 108° , but on mixing with this substance the melting point was $89-90^\circ$. We next prepared isobutyrylformamide, which again was quite similar in its properties. It melted at $107-108^\circ$, and this time the melting point remained unchanged, when the synthetic was mixed with the natural substance. The melting points may be tabulated thus:

1. Butyrylformamide, 108° . Mixture of 1 and 2, $88-89^\circ$.
2. Isobutyrylformamide, $107-108^\circ$. Mixture of 1 and 3, $89-90^\circ$.
3. Substance from ergot alkaloids, 109° . Mixture of 2 and 3, $107-108^\circ$.

In addition, the vapours of 2 and 3 readily gave, on gentle warming, the pyrrole reaction with a pinewood splint moistened with hydrochloric acid, but 1 gave only a doubtful coloration on strongly heating.

The sublimate from the ergot alkaloids is therefore isobutyrylformamide, $CHMe_2CO \cdot CO \cdot NH_2$.

In addition to this substance we obtained, on destructive distillation of the alkaloids under 2 mm. pressure, a small quantity of a base boiling at $88-89^\circ$, which was condensed in a tube cooled by carbon dioxide and acetone, and had an odour like pyrrolidine. The substance left in the flask was somewhat volatile under 2 mm. pressure, and crept up the sides of the flask as an amber-coloured, viscid liquid, but could not be distilled.

Synthesis of Butyryl and isoButyrylformamide.

Moritz (Trans., 1881, 39, 14) prepared butyryl and isobutyryl cyanide from the corresponding chlorides and silver cyanide. We found the yield to be very unsatisfactory, and therefore adopted Claisen's method (Ber., 1898, 31, 1023), using anhydrous hydrogen

cyanide. 12.5 Grams of butyryl chloride were added to a solution of 3.2 grams of hydrogen cyanide in 46 c.c. of dry ether, and to the well-cooled solution 10 c.c. of pyridine were slowly added. After standing overnight, the pyridine hydrochloride, which had separated, was removed by filtration. The ethereal filtrate was washed with 5 per cent. sulphuric acid to remove the pyridine, and then with water to remove the acid. After drying, the ethereal solution was evaporated, and the residue distilled, when 1 gram of butyrylcyanide was obtained; the rest of the reaction product consisted mostly of the bimolecular polymeride. By hydrolysis with 85 per cent. sulphuric acid, 0.4 gram of butyrylformamide was obtained. It was purified by sublimation from a boiling-water bath under diminished pressure, and melted in a sealed tube at 108° (Moritz found $105-106^{\circ}$). *iso*Butyrylformamide was prepared in the same way, and melted at $107-108^{\circ}$. As stated above, this substance, unlike the normal amide, on heating, readily gives the pyrrole reaction with pinewood. Its melting point is given by Moritz (erroneously) as $125-126^{\circ}$, by Brunner (*Monatsh.*, 1894, 15, 758) as $106-107^{\circ}$, and by Fränke and Kohn (*Monatsh.*, 1899, 20, 887) as 110° .

We desire to acknowledge our indebtedness to Messrs. E. T. Thompson and S. M. Pettet, who have respectively made the microphotographs and drawings, from which the figures of crystals have been prepared.

THE WELLCOME PHYSIOLOGICAL RESEARCH LABORATORIES,
BROCKWELL HALL, HERNE HILL, LONDON, S.E.

XXXI.—*The Action of Chlorine on Phenylcarbamide.*

By FREDERICK DANIEL CHATTAWAY and NEWCOMB KINNEY CHANEY.

THE action of chlorine on phenylcarbamide is of necessity a complicated one, since each of the three hydrogen atoms attached to nitrogen in the compound can be exchanged for halogen, which can also pass into the nucleus by intramolecular rearrangement when the hydrogen of the imino-group connecting the carbonyl and phenyl groups is replaced.

The isolation of the various compounds produced is rendered difficult and in some cases impracticable by the circumstance that the group $\cdot\text{CO}\cdot\text{NHCl}$, which is comparatively stable in presence of hydrochloric acid, at once breaks down with liberation of nitrogen in

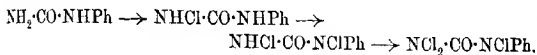
presence of alkali carbonates, whilst the group $\cdot\text{CO}\cdot\text{NCl}\cdot\text{C}_6\text{H}_5$, which is comparatively stable in presence of the latter, undergoes isomeric change under the influence of hydrochloric acid.

Hence, since chlorination has to be effected in acid solution, derivatives containing the unsubstituted phenyl residue, although undoubtedly formed, have not been isolated in a pure state; indeed, only when the phenyl group contains chlorine in all available positions can any considerable number of the *N*-halogen compounds theoretically possible be obtained.

The action of chlorine on phenylcarbamide is interesting, as the halogen passes with great ease at the ordinary temperature, not only into the para- but into both ortho-positions, whilst with acyl anilides the final transformation, in which the halogen enters the second ortho-position, is only effected with some difficulty at a comparatively high temperature.

The *N*-halogen derivatives obtained are also of more than ordinary interest on account of their unexpectedly great stability, for example, 2:4:6-trichlorophenyltrichlorocarbamide can be heated to a temperature approaching 130° without decomposition.

A consideration of the properties of the *N*-chloro-derivatives obtained leads to the conclusion that chlorine enters preferably the amino-group, the hydrogen of the $\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ group being next replaced thus :



The entrance of halogen into the nucleus follows the regular course the para- and ortho-positions being taken up, until finally all three are occupied by halogen.

EXPERIMENTAL.

Action of Chlorine and of Hypochlorous Acid on Phenylcarbamide.

The *N*-chloro-derivatives derivable from unsubstituted phenylcarbamide are undoubtedly formed when chlorine is passed into a solution of phenylcarbamide in glacial acetic acid containing an excess of sodium acetate, but halogen enters the phenyl group with such readiness that they have not been isolated. The considerable evolution of heat which takes place in this action is caused by the entrance of halogen into the ring, since only a very slight development of heat is caused by the replacement of hydrogen in carbamide by halogen.

If to a strongly-cooled solution of phenylcarbamide in alcohol the calculated quantity of *N*/10 aqueous hypochlorous acid is added, a *N*-chloro-derivative separates in the form of a somewhat viscid solid. This dissolves easily in chloroform, and is left on evaporation of the

solvent as a slightly brown, viscid mass, which, without doubt, consists mainly of the compound $\text{NCl}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4$, as it contains almost the theoretical amount of chlorine attached to nitrogen and is transformed into a mixture of substituted phenylcarbamides on keeping a solution in glacial acetic acid for some hours. We have not, however, succeeded in bringing it into a crystalline condition. Substituted *N*-chloro-derivatives, although crystallising well from chloroform or petroleum when perfectly pure, can only with great difficulty be made to crystallise when they contain even slight amounts of impurity, especially when, as in the case of those containing unsubstituted phenyl groups, they are of low melting point.

A similar result was obtained when phenylcarbamide suspended in water was chlorinated in presence of excess of calcium carbonate.

p-Chlorophenylchlorocarbamide, $\text{NHCl} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Cl}$.

This compound can be prepared by the careful chlorination of phenylcarbamide or of *p*-chlorophenylcarbamide dissolved in glacial acetic acid in presence of excess of sodium acetate. Five grams of *p*-chlorophenylcarbamide were dissolved in 250 grams of glacial acetic acid, and finely powdered, crystalline sodium acetate was added so long as it was dissolved. This liquid was cooled in ice to as low a temperature as possible without crystallisation of the glacial acetic acid, and a slow stream of chlorine passed in. *p*-Chlorophenylchlorocarbamide separated in small, colourless needles. The stream of chlorine was stopped before the whole of the *p*-chlorophenylcarbamide had been converted into the *N*-chloro-derivative, and the latter was collected, washed well with water and finally with chloroform, and dried in a vacuum over phosphoric oxide. It crystallises from warm chloroform, in which it is sparingly soluble, in colourless, fine needles. When heated it remains apparently quite unchanged until 122° , when it suddenly decomposes without previously melting. When treated with hydriodic acid, iodine is quantitatively liberated, and *p*-chlorophenylcarbamide, identical with that obtained from potassium cyanate and *p*-chloroaniline, is formed.

It and the other *N*-chloro-derivatives described in this paper were analysed by the method generally applicable to nitrogen chlorides, by adding known quantities to solutions of potassium iodide containing glacial acetic acid and titrating the iodine liberated with *N*/10-sodium thiosulphate:

0.1083 liberated iodine = 10.4 c.c. *N*/10 I. Cl as $\text{NCl} = 17.02$.

$\text{C}_7\text{H}_5\text{ON}_2\text{Cl}_2$ requires Cl as $\text{NCl} = 17.29$ per cent.

p-Chlorophenyldichlorocarbamide, $\text{NCl}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Cl}$.

This compound separates as a pale yellow solid when the calculated amount of an aqueous solution of hypochlorous acid is rapidly added to a solution of phenylcarbamide in glacial acetic acid. It crystallises from warm acetic acid, in which it is readily soluble, in pale yellow needles, which soften at about 85° and melt and decompose at about 90° :

0.1804 liberated iodine = 30.3 c.c. *N*/10 I. Cl as $\text{NCl} = 29.77$.

$\text{C}_7\text{H}_5\text{ON}_2\text{Cl}_2$ requires Cl as $\text{NCl} = 29.6$ per cent.

The yellow colour of the compound indicates that in it two chlorine atoms are attached to the same nitrogen atom.

p-Chlorophenyltrichlorocarbamide, $\text{NCl}_3 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Cl}$.

This compound is formed when chlorine in excess is passed into a cooled solution of *p*-chlorophenylcarbamide in glacial acetic acid in presence of excess of sodium acetate. The insoluble *N*-monochloro-derivative first formed slowly dissolves as the passage of the chlorine is continued, and the *N*-trichloro-derivative is obtained as a pale yellow, viscid liquid by diluting with water, extracting with chloroform, and removing the solvent in a current of dry air.

This liquid always gave on analysis a somewhat too low percentage of chlorine as NCl , and it has never been brought into a crystalline condition. This is probably due to it never having been obtained perfectly pure, but always mixed with a small amount of the corresponding *N*-trichloro-derivative of 2:4-dichlorophenylcarbamide, the passage of the chlorine having to be continued so long to effect the solution of the *N*-monochloro-derivative that transfer of chlorine into the phenyl group in the ortho-position always takes place to a small extent.

2:4-Dichlorophenylmonochlorocarbamide, $\text{NHCl} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_3\text{Cl}_2$.

This compound is formed when equivalent amounts of 2:4-dichlorophenylcarbamide and of its *N*-dichloro-derivative are dissolved in as small a quantity as possible of warm glacial acetic acid. On cooling, 2:4-dichlorophenylmonochlorocarbamide separates in needle-shaped crystals. It crystallises from hot chloroform, in which it is sparingly soluble, in long, colourless, silky needles. When heated it decomposes at 132° , giving off bubbles of gas and fusing to a brown mass:

0.2215 liberated iodine = 18.7 c.c. *N*/10 I. Cl as $\text{NCl} = 14.96$.

$\text{C}_7\text{H}_3\text{ON}_2\text{Cl}_2$ requires Cl as $\text{NCl} = 14.8$ per cent.

2:4-Dichlorophenyldichlorocarbamide, $\text{NCl}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_3\text{Cl}_2$.

2:4-Dichlorophenyldichlorocarbamide can be prepared either from phenylcarbamide or from *p*-chlorophenylcarbamide, and as it is easily soluble in chloroform and crystallises well, it can be separated without difficulty from any small admixture of other products which may be formed together with it.

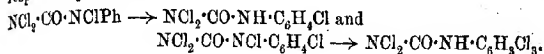
It is most readily prepared by dissolving phenylcarbamide in from twelve to fifteen times its weight of glacial acetic acid, adding two equivalents of powdered sodium acetate, and passing chlorine until the liquid is saturated. The liquid should be cooled as far as possible during the passage of the gas so that it never becomes even slightly warm. After filtering off, if necessary, a small quantity of 2:4:6-trichlorophenylmonochlorocarbamide, which is occasionally formed if the chlorination has been continued too long, cooled chlorine-water is added in excess, when the *N*-dichloro-derivative separates as a yellow solid or as a yellow liquid which quickly crystallises. To obtain it dry and free from adhering acid, it is best to add sufficient chloroform to dissolve it, shaking vigorously, then, after washing repeatedly with chlorine-water, separating, and drying the chloroform solution over fused calcium chloride, to drive off the solvent in a current of warm dry air. A yellow, crystalline solid separates as the chloroform volatilises, or if crystallisation does not at once take place, this can be brought about by stirring the deep yellowish-coloured oil with a little petroleum of very low boiling point. It can be similarly easily prepared from *p*-chlorophenylcarbamide or 2:4-dichlorophenylcarbamide, but as these are somewhat difficult to procure it is best to proceed as described above.

It crystallises well from hot chloroform, in which it is readily soluble, in pale yellow, four-sided, rhombic prisms. It melts at 76° ; when heated above this temperature, it remains apparently unchanged up to 100 – 105° , when it begins to give off gas; the gas evolution is at first very slight, but it increases in amount as the temperature rises until the neighbourhood of 120° is reached, when slight crackling explosions generally occur, due to the evolution and explosion of vapour of nitrogen chloride:

0.3897 liberated iodine = 56.8 c.c. $\text{N}/10 \text{ I}$. Cl as $\text{NCl} = 25.84$.
 $\text{C}_7\text{H}_4\text{ON}_2\text{Cl}_4$ requires Cl as $\text{NCl} = 25.88$ per cent.

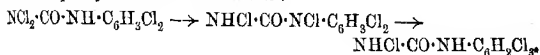
As this compound shows a yellow colour as intense as that of nitrogen chloride, it seems probable that both the chlorine atoms not in the nucleus are attached to the same nitrogen atom, since phenylcarbamide derivatives, which contain only one chlorine atom attached to nitrogen, and the dichloro-derivative of carbamide itself, which

contains two $\cdot\text{NHCl}$ groups, are without appreciable colour. It seems likely that this and the similarly-constituted derivative of *p*-chlorophenylcarbamide are formed by the intramolecular rearrangement of phenyltrichlorocarbamide and *p*-chlorophenyltrichlorocarbamide respectively, thus:



2:4-Dichlorophenyl-s-dichlorocarbamide, $\text{NHCl}\cdot\text{CO}\cdot\text{NCl}\cdot\text{C}_6\text{H}_3\text{Cl}_2$.

If 2:4-dichlorophenyldichlorocarbamide is dissolved in chloroform and the solvent allowed slowly to evaporate, tufts of slender, colourless prisms are deposited. These can be recrystallised from chloroform, but have never been obtained perfectly pure, as they readily change into 2:4:6-trichlorophenylmonochlorocarbamide, from which they cannot be completely freed. Different specimens were found to melt not very sharply about $80-85^\circ$, and to contain amounts of chlorine as $\cdot\text{NCl}$ varying from about 23.5 to 24.5 per cent., this being from 1 to 2 per cent. too low for the pure substance. Thus the coloured, unsymmetrical *N*-dichloro-derivative when in solution appears slowly to become converted into the colourless, symmetrical derivative, which very easily undergoes transformation into 2:4:6-trichlorophenylmonochlorocarbamide:



2:4:6-Trichlorophenylmonochlorocarbamide, $\text{NHCl}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_2\text{Cl}_3$.

This, on account of its stability and very sparing solubility in glacial acetic acid, is the most easily prepared of all the *N*-chloro-derivatives of phenylcarbamide. It is formed when either phenylcarbamide, *p*-chlorophenylcarbamide, or 2:4-dichlorophenylcarbamide is dissolved in acetic acid and chlorine passed into the liquid for any considerable period. It may be conveniently obtained as follows: Five grams of phenylcarbamide are dissolved in about 25 grams of glacial acetic acid, and a rapid stream of chlorine is passed into the solution, cooling by water so that the temperature does not rise above 20° . After the chlorine has been passing for an hour or thereabouts, fine colourless crystals of 2:4:6-trichlorophenylmonochlorocarbamide make their appearance in the liquid, and slowly increase in quantity as the passage of the gas is continued. When the separated solid no longer appears to increase in amount, it is collected and washed well with cold glacial acetic acid and afterwards with chloroform. A further quantity of a somewhat impure product can be obtained by adding a little

water to the filtrate. It crystallises from warm glacial acetic acid, in which it is sparingly soluble, in small, very slender, hair-like crystals. When heated it turns brown, and begins to decompose at about 150° , and, if rapidly heated, further melts and decomposes at about $155-156^{\circ}$. When dry, it can be kept for a long period at the ordinary temperature without decomposition:

0.2682 liberated iodine = 20.1 c.c. $N/10$ I. Cl as : $\text{NCl} = 13.28$.

$\text{C}_7\text{H}_5\text{ON}_2\text{Cl}_4$ requires Cl as : $\text{NCl} = 12.94$ per cent.

2 : 4 : 6-Trichlorophenylcarbamide, $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_2\text{Cl}_3$.

This compound is most easily obtained by replacing the *N*-halogen atom in 2 : 4 : 6-trichlorophenylmonochlorocarbamide by hydrogen.

Five grams of 2 : 4 : 6-trichlorophenylmonochlorocarbamide were suspended in 20 c.c. of glacial acetic acid, and 2 grams of powdered potassium iodide added. The iodine liberated was removed as fast as it was formed by adding an aqueous solution of sodium sulphite. When iodine was no longer liberated, a slight excess of sulphite solution was added, the liquid was warmed for some time on a water-bath, and kept for twenty-four hours. The 2 : 4 : 6-trichlorophenylcarbamide thus formed was then collected and recrystallised from alcohol. It separates from boiling alcohol, in which it is moderately easily soluble, in colourless, long, hair-like crystals. When heated rapidly it melts at 250° , and decomposes and evolves gas at a slightly higher temperature:

0.1422 gave 0.2545 AgCl . Cl = 44.24.

$\text{C}_7\text{H}_5\text{ON}_2\text{Cl}_3$ requires Cl = 44.42 per cent.

2 : 4 : 6-Trichlorophenyldichlorocarbamide, $\text{NHCl} \cdot \text{CO} \cdot \text{NCl} \cdot \text{C}_6\text{H}_3\text{Cl}_3$.

This and the *N*-trichloro-derivative are best obtained from pure 2 : 4 : 6-trichlorophenylcarbamide. Five grams of 2 : 4 : 6-trichlorophenylcarbamide were dissolved in 500 grams of cold glacial acetic acid, and a rapid stream of chlorine passed in for about ten minutes until the chlorine escaped freely. The clear yellow liquid thus produced was diluted with an equal bulk of water and extracted with chloroform. The chloroform solution was thoroughly washed with water, dried over fused calcium chloride, and the solvent driven off by a current of warm dry air. A very pale yellowish-coloured oily liquid was thus obtained, which on stirring with a little light petroleum deposited a white solid in fine granular crystals. This was recrystallised from hot chloroform, in which it is sparingly soluble, and separates in colourless, probably orthorhombic prisms terminated by dome or pyramidal faces. On being heated it remains apparently unchanged up to 128° , when it begins to decompose with crackling explosions without previously

melting. At this point chlorine is evolved, and it seems probable that the explosions are due to the liberation of the vapour of nitrogen chloride, which explodes as soon as it is formed, setting free chlorine.

0.2111 liberated iodine = 27.5 c.c. $N/10$ I. Cl as :NCl = 22.93.

$C_7H_5ON_2Cl_3$ requires Cl as :NCl = 22.99 per cent.

The circumstance that this compound is colourless leads to the conclusion that the two chlorine atoms attached to nitrogen are not attached to the same nitrogen atom, as does also its relatively high melting point.

2:4:6-Trichlorophenyltrichlorocarbamide, $NCl_2 \cdot CO \cdot NCl \cdot C_6H_2Cl_3$.

Four grams of 2:4:6-trichlorophenylcarbamide were mixed with about 8 grams of finely powdered sodium acetate and suspended in 50 grams of glacial acetic acid. The liquid was kept cool, and a slow stream of chlorine was passed in for an hour. The solution was then filtered, diluted with chlorine water, and extracted with chloroform. The chloroform extract was then repeatedly shaken with a cooled solution of chlorine water containing a little sodium acetate. On separating, drying with fused calcium chloride, and driving off the chloroform in a current of warm dry air, a deep yellowish-coloured, viscous liquid was obtained. On dissolving this in warm petroleum of low boiling point and keeping the solution for some hours, 2:4:6-trichlorophenyltrichlorocarbamide separated in bright yellow, short, glistening prisms.

It melts at 58° , and can be heated to 130° without apparent change. When heated above this temperature, bubbles of gas are liberated, and in the neighbourhood of 155° it darkens and completely decomposes:

0.2209 liberated iodine = 38.55 c.c. $N/10$ I. Cl as :NCl = 30.90.

$C_7H_2ON_2Cl_6$ requires Cl as :NCl = 31.02 per cent.

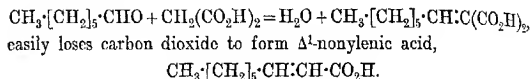
UNIVERSITY CHEMICAL LABORATORY,
OXFORD.

XXXII.— Δ^1 -Nonylenic Acid.

By VICTOR JOHN HARDING and CHARLES WEIZMANN.

In the present communication an account is given of the preparation in large quantities and the means of identification of Δ^1 -nonylenic acid, an acid of considerable technical importance. It was first obtained by Schneegans (*Annalen*, 1885, 227, 80), who prepared it by the condensation of heptaldehyde and sodium

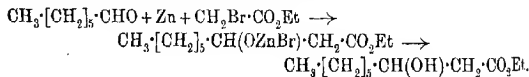
acetate by means of acetic anhydride at 160–170° for thirty hours. The yield was very poor, and its identification uncertain. Knevenagel (Friedländer: *Fortschritte der Teerfarbenfabrikation*, 7, 738) has also prepared this acid by the condensation of hept-aldehyde and malonic acid through the agency of piperidine. The authors, however, have not been able to obtain large yields by this method, the piperidine inducing condensation products of hept-aldehyde with itself similar in character to those obtained by means of alkalis. These high-boiling neutral products also occurred when other secondary or primary bases, such as diethylamine, ammonia, or aniline, were used as the condensing agent, and it was only when tertiary bases were employed that good yields of the desired acid were obtained. The heptylidenemalonic acid which is first obtained,



This unsaturated acid, after purification by means of its barium salt, boils at 144°/13 mm., and is obtained as a colourless oil with a characteristic odour. As a means of identification, the authors recommend the use of the amide or the *p*-toluidide, but more especially the former, as its preparation in a pure state is both easy and rapid. Δ^1 -Nonylenamide melts at 126–127°; the *p*-toluidide at 73–74°. The dibromo-acid,



although it has been obtained as a solid melting at 35°, on account of the difficulty with which it is prepared, is not suitable as a means of identification. Δ^1 -Nonylenic acid, on reduction with sodium and alcohol, gives nonyl alcohol. In order to control the constitution of the unsaturated acid, an alternative method of preparation was adopted. This was the condensation of hept-aldehyde and ethyl bromoacetate by means of zinc:



Ethyl β -hydroxy-*n*-nonoate, on hydrolysis, gives the corresponding acid as a white, crystalline solid, melting at 57–59°. This acid has previously been prepared by Wagner (*Ber.*, 1894, 27, 2736), who obtained it by the oxidation of hexylallylcarbinol by means of permanganate. Wagner gives the melting point of this acid as 48–51°, but we do not think there can be any doubt as to the identity of the two substances. The removal of water from the hydroxy-acid was accomplished by means of acetic anhydride, a

method which has been used with such conspicuous success by Wallach to produce unsaturated acids containing the ethylene linking in the $\alpha\beta$ -position. The identity of the two preparations of Δ^1 -nonylenic acid was proved by means of their amides, a mixture of the two preparations having the same melting point as their separate constituents.

EXPERIMENTAL.

Δ^1 -Nonylenic Acid, $\text{CH}_3[\text{CH}_2]_7\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$.

After many unsuccessful attempts, the following method of preparing Δ^1 -nonylenic acid was found to give the best results. One hundred grams of malonic acid were dissolved in 160 grams of pyridine, and to the cold liquid was added 100 grams of heptaldehyde. The whole was kept at the ordinary temperature for thirty-six hours, and then gently heated on the water-bath for two hours. The product was poured into water, and acidified with hydrochloric acid. The oil was extracted by ether, and well washed with water. The unsaturated acid was next removed from the ethereal extract by means of sodium carbonate solution. The ethereal solution was dried and evaporated, when the very small residue which was obtained was found to consist almost entirely of unchanged heptaldehyde, high condensation products being produced only in very small amount. The sodium carbonate washings, on acidification, extraction with ether, drying, and distillation, yielded 90 grams of Δ^1 -nonylenic acid, boiling at $145\text{--}150^\circ/12\text{ mm}$. Analyses of this acid, even on redistillation, always showed a deficiency of carbon, and several methods of purification were tried, of which the following gave the best results. Eighty grams of the distilled acid were boiled in 95 per cent. alcohol with 127 grams of pure barium hydroxide. The barium salt which is formed gradually dissolves in much boiling alcohol, from which it separates on cooling as a white, crystalline powder. This, on acidifying with dilute hydrochloric acid and extraction with ether, gave about 40 grams of pure Δ^1 -nonylenic acid, boiling constantly at $144^\circ/13\text{ mm}$.

0.1210 gave 0.3097 CO_2 and 0.1102 H_2O . $\text{C}=69.7$; $\text{H}=10.1$.

$\text{C}_9\text{H}_{16}\text{O}_2$ requires $\text{C}=69.2$; $\text{H}=10.2$ per cent.

Δ^1 -Nonylenic acid is a colourless oil, with the faint odour characteristic of acids of this class. It is readily soluble in cold sodium carbonate solution, and instantly decolorises cold alkaline permanganate. The preparation of Δ^1 -nonylenic acid in good yield was also attempted by condensing heptaldehyde and malonic acid by the use of piperidine (Knevenagel, *loc. cit.*), but the yields were

very poor, large amounts of high-boiling condensation products of heptaldehyde with itself being formed. This is easily shown if to heptaldehyde alone a few drops of piperidine are added. The liquid rapidly becomes hot, loses the characteristic odour of heptaldehyde, and decomposes on distillation. Similar results are given by other primary and secondary bases, such as ammonia, aniline, and diethylamine. The condensation of heptaldehyde and malonic acid by means of dimethylaniline gave, from 100 grams of heptaldehyde, 30 grams of Δ^1 -nonylenic acid and also some condensation products of high boiling point. These we attribute to the presence of methylaniline in the dimethylaniline employed.

Δ^1 -Nonylenyl Chloride.—Nonylenic acid reacts vigorously with phosphorus pentachloride to form Δ^1 -nonylenyl chloride, boiling at $144^\circ/90$ mm.:

0.2861 gave 0.2335 AgCl. Cl=19.9.

$C_9H_{15}OCl$ requires C=20.1 per cent.

The methyl and ethyl esters boil respectively at $110^\circ/20$ mm. and $123^\circ/25$ mm.

Δ^1 -Nonylenamide, $C_8H_{15}CO \cdot NH_2$.—This most characteristic derivative of Δ^1 -nonylenic acid is very readily prepared by pouring the acid chloride into concentrated aqueous ammonia. The amide instantly separates as a solid, and is collected and purified by crystallisation from aqueous methyl alcohol or petroleum. It crystallises in beautiful pearly leaflets, melting at $126-127^\circ$.

0.1741 gave 13.9 c.c. N_2 (moist) at 20° and 752 mm. N=9.0.

$C_9H_{17}ON$ requires N=8.9 per cent.

*Δ^1 -Nonyleno-*p*-toluidide* is prepared by adding the acid chloride to a slight excess of *p*-toluidine and then gently warming. The yellow, semi-solid mass which is produced is then treated several times with dilute hydrochloric acid and with sodium carbonate solution. The adhering oil is removed by contact with porous porcelain, and leaves the *p*-toluidide as a white solid, which crystallises from light petroleum in small, shining leaflets melting at $73-74^\circ$:

0.1610 gave 7.6 c.c. N_2 (moist) at 19° and 770 mm. N=5.5.

$C_{16}H_{25}ON$ requires N=5.7 per cent.

β -Hydroxy-n-nonoic Acid and its Ester,
 $CH_3[CH_2]_6CH(OH) \cdot CH_2 \cdot CO_2H.$

This acid is easily and rapidly prepared by condensing heptaldehyde and ethyl bromoacetate by means of zinc in benzene solution. Eighty-eight grams of heptaldehyde and 128 grams of ethyl bromoacetate are mixed with twice their volume of benzene,

and 52 grams of zinc added. The reaction is started by warming on the water-bath, but when once commenced is extremely vigorous, and cooling must be resorted to. When the reaction has subsided, the condensation may be completed by heating on the water-bath for a couple of hours. The viscous product is decomposed by ice and hydrochloric acid, extracted with ether, the ethereal extract well washed with water, dried, and distilled, when ethyl β -hydroxy-nonoate passes over as a colourless, inodorous oil, boiling at $145^\circ/13$ mm.:

0.1381 gave 0.3302 CO_2 and 0.1287 H_2O . $\text{C}=65.2$; $\text{H}=10.4$.

$\text{C}_{11}\text{H}_{22}\text{O}_2$ requires $\text{C}=65.3$; $\text{H}=10.8$ per cent.

When treated with an aqueous solution of hydrogen bromide saturated at 0° , this hydroxy-ester only gives very small quantities of ethyl β -bromo-nonoate, the hydroxy-group remaining unaffected. β -Hydroxy-n-nonoic acid is easily obtained by the hydrolysis of its ester by means of alcoholic potash. The potassium salt, which separates in large plates from the alcoholic solution on cooling, is collected, dissolved in a little water, cooled with ice, and acidified, when β -hydroxy-n-nonoic acid separates as an oil which rapidly solidifies. This is collected, any adhering oil being removed by contact with porous porcelain, and purified by crystallisation from hot water, or from light petroleum, when it melts at $57-59^\circ$:

0.1193 gave 0.2707 CO_2 and 0.1102 H_2O . $\text{C}=61.9$; $\text{H}=10.2$.

$\text{C}_9\text{H}_{16}\text{O}_3$ requires $\text{C}=62.1$; $\text{H}=10.3$ per cent.

β -Hydroxy-n-nonoic acid crystallises in short needles as a white, inodorous compound. It is readily soluble in cold benzene, alcohol, chloroform, acetic acid, or ethyl acetate, and is stable towards cold alkaline permanganate. It is instantly soluble in cold sodium carbonate solution. When treated with an acetic acid solution of hydrogen bromide and gently warmed, it yields β -bromo-n-nonoic acid as a heavy oil.

Preparation of Δ^1 -Nonylenic Acid from β -Hydroxy-n-nonoic Acid.

In order to confirm the constitution of Δ^1 -nonylenic acid prepared from heptaldehyde and malonic acid, it was deemed advisable to prepare it from β -hydroxy-n-nonoic acid, using acetic anhydride as a dehydrating agent. Ten grams of crude β -hydroxy-n-nonoic acid were boiled with 50 c.c. of acetic anhydride for four hours. The product was poured into water, and distilled in a current of steam, when the unsaturated acid passed over slowly. The distillate was saturated with ammonium sulphate, extracted with ether, and frac-

tionated under diminished pressure, when the acid (5 grams) was found to boil at $181^\circ/60$ mm.:

0.1315 gave 0.3293 CO_2 and 0.1237 H_2O . $\text{C}=68.3$; $\text{H}=10.4$.

$\text{C}_9\text{H}_{16}\text{O}_2$ requires $\text{C}=69.2$; $\text{H}=10.2$ per cent.

The acid prepared in this way possessed a sharper odour than that prepared by the first method, but its identity was proved beyond all doubt by its conversion into the acid chloride and then into the amide. The amide, when crystallised from petroleum, melted at 126° , and when mixed with a specimen of Δ^1 -nonylenamide prepared from malonic acid, no alteration in the melting point was observed.

Reduction of Ethyl Δ^1 -Nonylenate to Nonyl Alcohol.

Fifty grams of ethyl nonylenate, prepared from the crude acid, are dissolved in 150 grams of absolute alcohol, and gradually added to 50 grams of sodium contained in a large flask provided with a reflux condenser, the temperature being kept at 150° . The reduction is very vigorous, and alcohol must be added from time to time to complete the solution of the sodium. When all the sodium has dissolved, the product is distilled in a current of steam, the nonyl alcohol being extracted by ether and fractionated. The yield is 35 per cent. The nonyl alcohol was identified by means of its phenylurethane.

$\alpha\beta$ -Dibromo- n -nonoic Acid, $\text{CH}_3[\text{CH}_2]_7\text{CHBr}\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$.

This acid is prepared by the addition of bromine to a solution of Δ^1 -nonylenic acid in carbon disulphide until the bromine ceases to be decolorised. The carbon disulphide is distilled off, the acid dissolved in ether, washed with dilute sulphurous acid, dried, and the ether evaporated. After a long time in an evacuated desiccator, the yellow oil gradually solidifies to a white, crystalline solid. This is pressed on porous porcelain to remove adhering oil, but the acid is too soluble in all organic solvents to permit of a convenient crystallisation. It melts at 35° :

0.2125 gave 0.2450 AgBr . $\text{Br}=49.1$.

$\text{C}_9\text{H}_{16}\text{O}_2\text{Br}_2$ requires $\text{Br}=50.6$ per cent.

It is soluble in dilute sodium carbonate solution, but the solution rapidly becomes cloudy, owing to the separation of α -bromo- Δ^1 -nonylenic acid.

XXXII.—*Strychnine, Berberine, and Allied Alkaloids*;

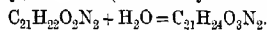
By WILLIAM HENRY PERKIN, JUN., and ROBERT ROBINSON.*

I.—*Strychnine and Brucine*.

SEVERAL years ago (Trans., 1889, 55, 63; 1890, 57, 992) one of us carried out a systematic study of the alkaloid berberine, and succeeded in obtaining a series of degradation products, the investigation of which made it possible to suggest a constitutional formula for berberine, and this formula, except for slight modifications in minor details, is still accepted as correct. The intention at that time was to use the experience obtained in order to attack the problem of the constitutions of several other alkaloids, and afterwards to attempt their synthesis, and a series of experiments on cryptopine* (Proc., 1891, 7, 166) and on other opium alkaloids were commenced.

Owing, however, to the necessity for completing other investigations, these researches had, for the time, to be reluctantly put aside.

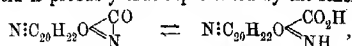
In recent years the difficult problem of the constitution of brazilin and hæmatoxylin made it imperative that we should very carefully study the constitution and nature of the groupings contained in natural products generally, and particularly in the alkaloids, and, in reviewing the work which had been published on strychnine, brucine, berberine, corydaline, and allied alkaloids, we were led to certain conclusions as to their constitutions which we think may be worth recording, and the validity of which we propose to test by experiment. Although the alkaloids, strychnine and brucine, have been the subject of detailed investigations, especially at the hands of Tafel and Leuchs, very few deductions have been made as to their constitutions. It is well known that strychnine, $C_{21}H_{22}O_3N_2$, while containing two atoms of nitrogen, is only a mon-acid base, yielding salts, such as the hydrochloride, $C_{21}H_{22}O_3N_2.HCl + 1\frac{1}{2}H_2O$, with only one equivalent of the acid. It is also known that the alkaloid is a tertiary base, and that it does not contain methoxy-groups. When strychnine is treated with alkalis (Loebisch and Schoop, *Monatsh.*, 1886, 7, 75; Tafel, *Annalen*, 1891, 264, 49), it suffers hydrolysis with the addition of a molecule of water and formation of strychnic acid (and isostrychnic acid, p. 317):



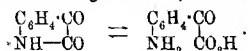
Strychnic acid is an imino-carboxylic acid, and at the same time

* Owing to the generosity of Messrs. T. and H. Smith, of Edinburgh, who have supplied me with considerable quantities of this very rare alkaloid, this investigation is being continued.—W.H.P., jun.

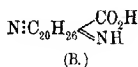
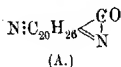
a tertiary base, since it yields metallic salt, and, when treated with methyl iodide, is converted into methylstrychnic acid methiodide, $C_{20}H_{22}ON(MeI)(NMe) \cdot CO_2H$ (Tafel, *Annalen*, 1891, 284, 59), and the presence of the imino-group is further demonstrated by the formation of a nitrosamine, $C_{20}H_{22}ON(N \cdot NO) \cdot CO_2H$, when the acid is treated with nitrous acid. These results, together with the fact that strychnic acid is readily converted into strychnine by heat, led Tafel to suggest that the relationship of strychnine to strychnic acid is probably that represented by the scheme:



and is similar to that existing between ψ -isatin and isatinic acid:

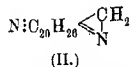
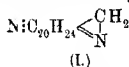


It can scarcely be doubted that this representation is correct, and the non-basic properties of the grouping $\cdot CO \cdot N \cdot$ affords an explanation of the fact that strychnine, although it contains two nitrogen atoms, is only capable of combining with one equivalent of an acid. Further confirmation of the presence of the grouping $\cdot CO \cdot N \cdot$ in strychnine is obtained from the study of the products which are formed when the alkaloid is treated with various reducing agents. When strychnine is reduced with phosphorus and hydriodic acid, it is converted into a substance, $C_{21}H_{29}ON$, called desoxystrychnine (Tafel, *Annalen*, 1892, 268, 245), and this substance, the importance of which is emphasised in the following pages, evidently has the formula (A):



since, like strychnine itself, it is a mon-acid base, which, on hydrolysis, yields desoxystrychnic acid (B).

This imino-acid has properties very similar to those of strychnic acid, and its whole behaviour indicates that the characteristic groups $N \cdot$ and $\cdot CO \cdot N \cdot$ of strychnine have undergone no change during the reduction to desoxystrychnine. When desoxystrychnine is treated with sodium and alcohol, it yields strychnoline (I), the $\cdot CO \cdot N \cdot$ group becoming $\cdot CH_2 \cdot N \cdot$, but electrolytic reduction proceeds further and, causes the addition of another two atoms of hydrogen, and dihydrostrychnoline (II) results (Tafel, *Annalen*, 1898, 301, 324 and 326):



Lastly, when strychnine itself is reduced, electrolytically, it yields

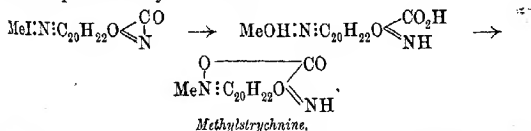
strychnine (III) the group $\cdot\text{CO}\cdot\text{N}\cdot$ being reduced to $\text{H}_2(\text{OH})\text{N}\cdot$, and this readily loses water with formation of trychnidite (IV) (Tafel, *Annalen*, 1898, 301, 303):



One of the most characteristic properties of strychnine is the ease with which it is nitrated, since warming with very dilute nitric acid (5 per cent.) converts it into dinitrostrychnine hydrate, $\text{H}_2\text{O}\cdot\text{N}_2(\text{NO}_2)_2\cdot\text{H}_2\text{O}$ (Tafel, *Annalen*, 1898, 301, 299).

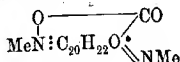
This behaviour, and also the fact that strychnine is very readily alphonated (Leuchs and Schneider, *Ber.*, 1909, 42, 2681), may be taken as proof of the presence of at least one benzene ring, and will be shown later that all the evidence points to there being only one such ring in the molecule. There can, furthermore, be little doubt that this benzene ring forms part of a quinoline nucleus, and, although no known quinoline derivative has so far been obtained from strychnine, there is ample indirect evidence of the presence of such a nucleus.

Tafel (*Annalen*, 1898, 301, 336) investigated the action first of dilute and then of strong nitric acid on strychnine, and showed that, under the conditions he employed, the alkaloid is nitrated and suffers degradation with the formation of dinitrostrychnol-carboxylic acid, $(\text{NO}_2)_2\text{C}_9\text{H}_2\text{N}(\text{OH})_2\cdot\text{CO}_2\text{H}$, and this important acid, when heated at 200° , loses carbon dioxide, with the formation of dinitrostrychnol, $(\text{NO}_2)_2\text{C}_9\text{H}_2\text{N}(\text{OH})_2$. There can be little doubt, as, indeed, Tafel has suggested, that this latter substance is a dinitrodihydroxyquinoline, and we are at present engaged in its investigation, not only with the object of proving this point, but also, at the same time, of determining the relative positions of the substituent groups in the quinoline nucleus. Still more conclusive evidence of the presence of the quinoline nucleus in strychnine has been obtained in the following way. Strychnine combines with methyl iodide to yield strychnine methiodide, $\text{C}_{21}\text{H}_{23}\text{O}_2\text{N}_2\cdot\text{MeI}$, and this, on treatment with silver hydroxide, or barium hydroxide, yields methylstrychnine, and, since this substance shows all the properties of a betaine, there can be little doubt that its formation is to be represented by the scheme:

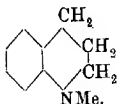


Methylstrychnine has all the properties of a secondary base; it

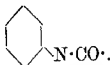
yields, for example, a nitrosamine, and reacts with methyl iodide to form dimethylstrychnine:



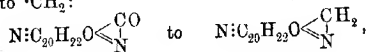
Tafel (*Annalen*, 1891, 264, 43) has already pointed out how remarkably the properties of dimethylstrychnine resemble those of *N*-methyltetrahydroquinoline:



and dimethylaniline. Like these substances, dimethylstrychnine yields a green nitroso-derivative, and condenses with benzaldehyde in the presence of zinc chloride with the formation of the leuco-base of a green colouring matter, which closely resembles malachite-green and the green colouring matter obtained from *N*-tetrahydroquinoline under the same conditions; furthermore, it combines with diazobenzenesulphonic acid to yield a yellow azo-dye. Because of this behaviour, Tafel draws the conclusion, not only that strychnine contains a quinoline nucleus, but also that the :NMe group in dimethylstrychnine and the :NH group in methylstrychnine, and therefore the :N·CO· group in strychnine, is combined by one linking direct to the benzene ring, and that strychnine must therefore contain the grouping:



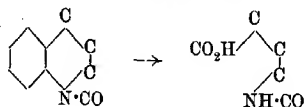
The consideration of the properties of strychnidine leads to exactly the same conclusions. This substance is produced, as explained on p. 307, by the reduction of the CO· group in strychnine to ·CH₂:



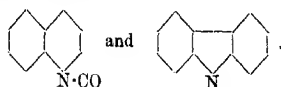
and this process converts a substance with the properties of acetanilide into one which again exhibits exactly the behaviour of dimethylaniline or *N*-methyltetrahydroquinoline towards reagents.

The most valuable evidence as to the internal structure of the other portion of the strychnine molecule is obtained from the consideration of the properties of an important monobasic acid, C₁₅H₁₇O₂N₂·CO₂H, which is produced when strychnine is oxidised by chromic acid (Hanssen, *Ber.*, 1884, 17, 2849; 1885, 18, 777 and 1917; 1887, 20, 451). This acid is also obtained under the same conditions from brucine, an alkaloid which contains two

methoxy-groups and has properties so exactly similar to those of strychnine that there can be no doubt that it is dimethoxy-strychnine. Since the two methoxy-groups disappear during the formation of the acid $C_{15}H_{17}O_2N_2 \cdot CO_2H$ from brucine, it follows that the benzene ring of the quinoline nucleus in the two alkaloids, brucine and strychnine, is broken down during the formation of this acid, evidently in the following manner:



Now the acid $C_{15}H_{17}O_2N_2 \cdot CO_2H$ is a derivative of carbazole, because it yields this substance on distillation with zinc dust, and we therefore arrive at the conclusion that the molecule of strychnine must contain the two residues:

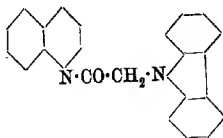


It has already been shown that the quinoline nucleus contains a benzene ring, and therefore, in order to account for the large number of hydrogen atoms in the strychnine molecule, it is necessary, as it appears to us, to conclude that not only the pyridine ring of the quinoline nucleus, but also the carbazole section of the molecule must be almost completely reduced. Adopting a line of argument which we have employed on previous occasions (Trans., 1890, 57, 1004; 1902, 81, 238; 1908, 93, 491), we find that these facts afford a basis on which it is possible to build up constitutional formulae for strychnine and its derivatives which, we are convinced, must at least be very near the truth.

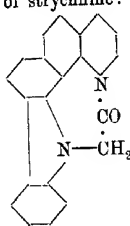
The two residues just figured contain C_{22} , and as the formula of strychnine is $C_{21}H_{22}O_2N_2$, it follows that these two residues must be fused together in such a way that one carbon atom at least is common to both. It is clear that the basic nature of strychnine is not due to the nitrogen atom of the tetrahydroquinoline nucleus, because of its union with the CO group; it must therefore be due to the nitrogen atom of the carbazole residue. If we now attempt to construct a formula for strychnine on the assumption that the two residues are united in such a way that one carbon atom is common to both, we have to remember that strychnine is a tertiary base, and the nitrogen of the reduced carbazole residue must therefore be rendered tertiary by union with a carbon atom of the quinoline nucleus, whilst the CO group unites with the carbazole

nucleus. This would lead to a formula which clearly cannot represent the skeleton of strychnine.

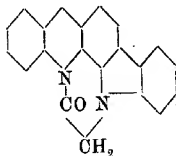
It seems to us that the only possible alternative is to assume that, in the fusion of the two nuclei, two carbon atoms become common to both,* and that the skeleton, which now contains C_{20} , is completed by the introduction of an additional carbon atom between the CO group and the basic nitrogen atom,† yielding, in the first place:



Further fusion may now take place in two ways, and two only; and leads us to the following alternative expressions for the skeleton of strychnine:

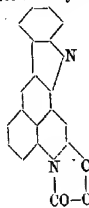
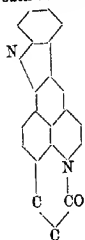


(I.)



(II.)

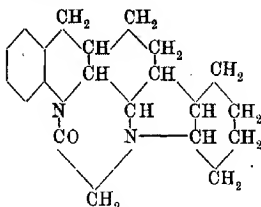
* If the two nuclei are fused together in such a way that three carbon atoms are common to both, then two additional carbon atoms must be introduced, and we obtain expressions such as the following for the skeleton of strychnine:



In such cases the carboxylic group in strychnic acid methiodide would be so far removed from the iodine atom that the formation of a betaine would appear to be out of the question (p. 307).

† For, if not, then the only other possible way of uniting the $N-CO$ group with the rest of the molecule, in order to make the basic nitrogen atom tertiary, is the construction of a four-carbon ring, which is highly improbable.

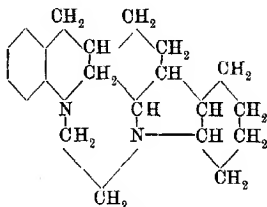
Formula I contains a seven-membered ring, and it is very unlikely that such a ring would be readily produced by the elimination of water from strychnic acid; on the other hand, such elimination leading to the formation of a six-membered ring is quite usual, and for this and other reasons we prefer formula II. If this formula be accepted as the skeleton of strychnine, there can be little doubt that desoxystrychnine, $C_{21}H_{28}ON_2$, the product of the reduction of strychnine with phosphorus and hydriodic acid (p. 306), must be written:



Desoxystrychnine.

and this formula is in complete agreement with the properties of this substance. It exhibits desoxystrychnine as a derivative of tetrahydroquinoline, accounts for its conversion into desoxystrychnic acid, and for the behaviour of this acid, as well as of desoxystrychnine itself, towards methyl iodide, nitrous acid, etc.

Similarly, the highest product of the hydrogenation of strychnine, namely, dihydrostrychnoline, $C_{21}H_{28}N_2$ (p. 306), will be represented by the formula:

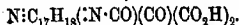


Dihydrostrychnoline.

and the fact that further hydrogenation, without reduction of the benzene ring, is impossible is well indicated by this structure.

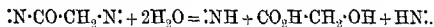
On the basis of skeleton formula II, it is possible not only to explain the recent important results of Leuchs (*Ber.*, 1908, **41**, 1711), Leuchs and Schneider (*ibid.*, 4393; 1909, **42**, 2494), and Leuchs and Weber (*Ber.*, 1909, **42**, 3703), but also to deduce a constitutional formula for strychnine which cannot be very far from the truth.

Leuchs and his collaborators find that strychnine, on oxidation in acetone solution with permanganate, is converted into a keto-dibasic acid, strychninonic acid, which has the composition,



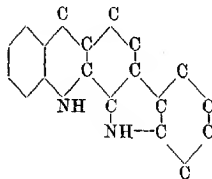
On reduction with sodium amalgam, this acid yields the corresponding secondary alcohol dibasic acid, strychninolic acid, $\text{N:C}_{17}\text{H}_{18}(\text{N}\cdot\text{CO})(\text{CH}\cdot\text{OH})(\text{CO}_2\text{H})_2$, and this substance, on treatment with dilute potassium hydroxide, is decomposed, yielding glycollic acid and strychninolone, $\text{C}_{19}\text{H}_{16}\text{O}_3\text{N}_2$, a substance which possesses neither acid nor basic properties. An exactly similar series of products was also obtained from brucine under the same conditions.

There can be no doubt that the formulæ for strychninonic and strychninolic acids suggested by Leuchs, which represent these acids as containing a tertiary nitrogen atom, are correct, and the absence of basic properties is amply explained by the presence of the two carboxyl groups. When strychninolic acid loses glycollic acid under the influence of alkali, the substance produced, strychninolone, is devoid of both acid and basic properties, and it is therefore obvious that, during its formation, mutual neutralisation has taken place between the two carboxyl groups and basic nitrogen atoms. Since two such atoms are required for this process, it follows that the section $\text{N}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{N}\cdot$ of the original strychnine skeleton must have lost the grouping $\cdot\text{CO}\cdot\text{CH}_2\cdot$, and this is therefore the source of the glycollic acid:

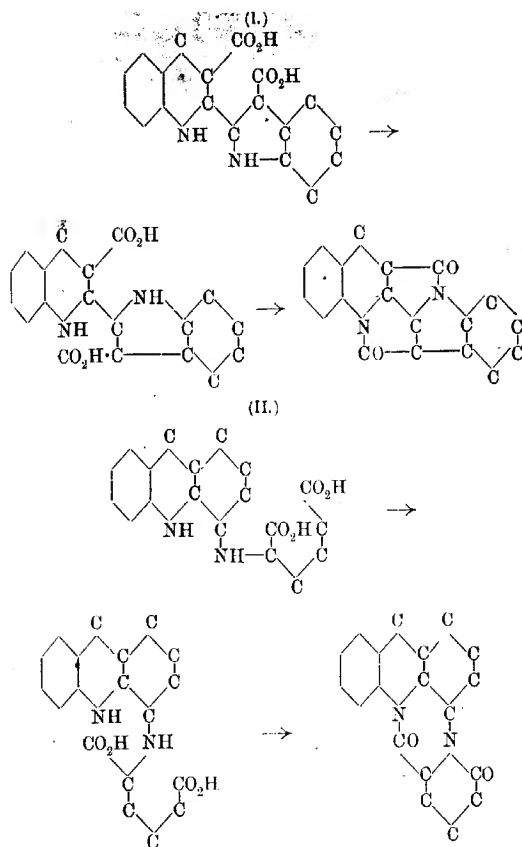


The cause of the non-basic nature of one of the nitrogen atoms in strychnine is thus removed, and the two NH groups are now both basic and free to combine with two carboxyl groups to yield a neutral substance, such as strychninolone.

The problem which still remains is to discover the process by which the structure:

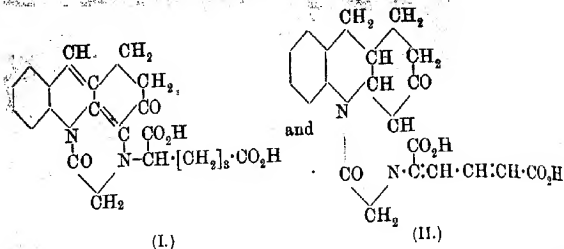


can be broken up in order to supply two carboxyl groups in such positions that they can combine with the two NH groups to yield two neutral $\text{N}\cdot\text{CO}\cdot$ groupings. The following appear to be the only two ways in which this can be satisfactorily accomplished:



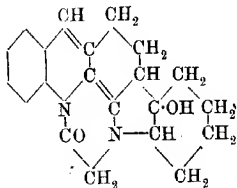
If now the hydrogen atoms and the carboxyl and other groups in strychninonic acid, $N:C_{17}H_{18}(N \cdot CO)(CO)(CO_2H)_2$, are filled into the first formula of scheme I, it will be found that the complete expression must contain one double linking, whereas, if the same process is carried out in the case of scheme II, two double linkings will be found to be necessary. This difference is due to the fact that, in developing scheme I from the skeleton formula of strychnine, one closed ring suffers fission, whereas in the case of scheme II two closed rings suffer disruption.

If we consider, in the first place, the development of a formula for strychninonic acid on the basis of the first skeleton formula of scheme II, we arrive at expressions of the types



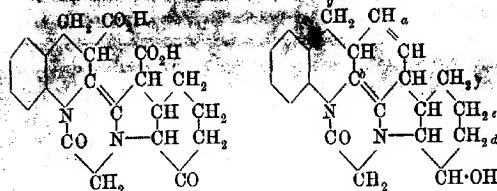
It can be shown in several ways that such formulae cannot represent strychninonic acid, and the same is true of any other formulae built up on the basis of the first skeleton formula of scheme II, but only one reason for this need be given here.

Strychninonic acid is obtained from strychnine by a simple permanganate oxidation, and it must therefore be possible to reconstruct the formula of strychnine in a comparatively simple manner from that of strychninonic acid. If we select formula I, and attempt to construct from it a formula for strychnine, we arrive at the expression:



which cannot be correct, because oxidation with permanganate would attack the double linking combined with the benzene ring, and it would therefore be impossible to obtain from this expression the formula for strychninonic acid from which it was derived, and the same line of argument applies equally to all other formulae derived from the first skeleton formula of scheme II.

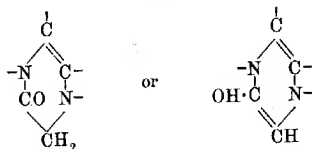
Whilst, then, scheme II is out of the question, careful consideration shows that scheme I leads to the following expressions for strychninonic acid and strychnine:



Strychninonic acid.

Strychnine.

which seem to us to be in every way satisfactory, since they account in a comparatively simple manner for all the known reactions of these substances. From the several possibilities we were led to select the positions assigned to the double linkings in the strychnine formula for various reasons, and of these the following need only be discussed. If the formula assigned to strychninonic acid is correct, the formation of this acid by the oxidation of strychnine clearly points to one of the double linkings occupying the position marked *a*. The position *b* was selected for the second double linking, because this linking must be situated in a stable portion of the molecule, otherwise it would also suffer oxidation under the conditions employed in the preparation of strychninonic acid, and experience of heterocyclic systems has shown that the double linkings in nuclei, such as:



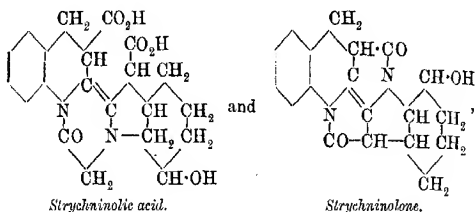
are not readily oxidised. Strychninonic acid is a keto-dibasic acid, and there can be little doubt that the keto-group is produced by the oxidation of a secondary alcohol group; in other words, the molecule of strychnine contains a $\text{CH}(\text{OH})$ group (compare Leuchs, *Ber.*, 1908, 41, 1711), and the difficult problem remaining to be solved is that of assigning the correct position to this group.

It cannot occupy the position *g*, because this would make strychninonic acid a derivative of benzoylactic acid, and *f* and *e* seem also to be out of the question, for the reason that hydroxy-groups in these positions would be γ - and δ - to one of the carboxyl groups in strychninonic acid, and this acid does not appear to have any tendency to yield a lactone. So far no definite experimental evidence is available to enable us to select with any certainty either of the remaining positions *d* or *c*, but we have

chosen *c* as the result of a comparison of strychnine with quinine and other natural products in which a similar grouping occurs.

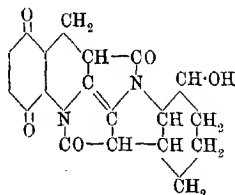
This argument, based on lactone formation, might appear to apply also to a hydroxyl group in the position *c*, but the examination of a model shows that a hydroxyl group in this position is too far removed from the carboxyl group to make lactone formation probable.

The formula which we have suggested for strychninonic acid leads to the following expressions for strychninolic acid and strychninolone:

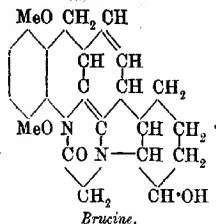


and these also appear to agree in a satisfactory manner with the properties of these substances so far as they have been investigated. A possible objection to the formula assigned to strychninolone is the stability of this substance towards oxidising agents, which may not be considered compatible with the presence of the CH-OH group, but, in our opinion, this argument does not carry much weight.

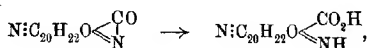
It has already been pointed out (p. 309) that brucine is di-methoxystrychnine, and the positions of the methoxy-groups in the benzene nucleus seem to be fixed by the observation of Leuchs and Weber (*Ber.*, 1909, 42, 3709) that brucinolone is readily oxidised by nitric acid, with elimination of the methoxy-groups and formation of a quinone which crystallises in red needles, and yields a quinol on reduction with sulphurous acid. Since an *o*-quinone would hardly be produced under these conditions, it is probable that the substance is a *p*-quinone of the constitution:



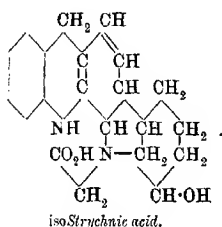
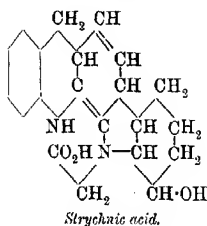
and its formation is a strong indication that the methoxy-groups occupy the position assigned to them in the following formula for brucine:



One other very interesting point in connexion with strychnine and brucine which we have already mentioned (p. 305) is the behaviour of these alkaloids on hydrolysis. When strychnine is digested with sodium methoxide or barium hydroxide, it yields strychnic and isostrychnic acids:

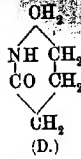
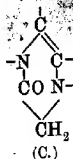


and these isomeric acids are converted by the action of heat into the isomeric alkaloids, strychnine and isostrychnine. Brucine exhibits an exactly similar behaviour. Strychnic and isostrychnic acids resemble each other so closely in all their reactions that it might at first sight appear that they were simply stereoisomeric modifications of the same substance. The conversion of these acids into the isomeric strychnines is, however, scarcely in accordance with this view, and it is far more probable that the isomerism is due to a difference in the position of one of the double linkings in the molecule, probably in the sense represented by the formulæ:



If the formulæ suggested for strychnine and brucine be examined with the view of discovering some reason for the extremely poisonous

nature of these alkaloids, it would seem that the only section to which this property can be ascribed is the grouping (C):

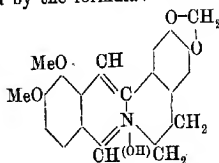


containing the two nitrogen atoms. Schotten (*Ber.*, 1888, 21, 2244) has called attention to the fact that α -ketopiperidine (α -piperidone) (D) has poisonous properties of the same kind as those exhibited by strychnine and brucine, and it is not at all improbable that the introduction of the second nitrogen atom into this molecule may have the effect of much intensifying these poisonous properties.

We are at present engaged in synthesising substances containing the above di-nitrogen group, and propose to have these examined in order to find out whether they have poisonous properties similar to those of strychnine and brucine.

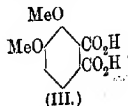
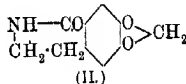
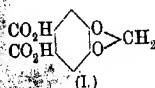
II.—Berberine, Corydaline, and Allied Alkaloids.

The constitution of berberine, $C_{20}H_{17}O_4N$, is generally accepted as being represented by the formula:



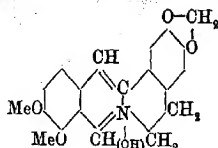
and this formula is based on the investigation of the long series of products which result from the degradation of the molecule by oxidation with permanganate (*Trans.*, 1889, 55, 63; 1890, 57 992).

The position of the methylenedioxy-group * is determined by the fact that hydrastic acid (I) and ω -aminoethylpiperonylcarboxyl anhydride (II) are found among the products of this oxidation:



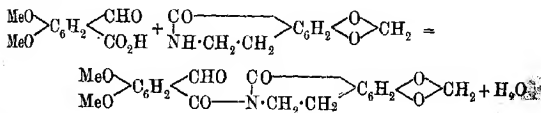
* It is unfortunate that this group should have been wrongly placed in the original papers.—W. H. P., jun.

On the other hand, the fact that hemipinic acid (III) is produced in considerable quantities during the oxidation of berberine does not definitely fix the positions of the methoxy-groups, since the formula for berberine:

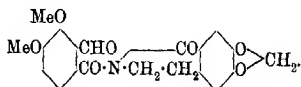


would also account for the formation of hemipinic acid on oxidation.

On carefully considering this matter, it appeared to us that the only oxidation product of berberine which is able to afford definite information as to the position of these methoxy-groups is *berberal* (Trans., 1890, 57, 1000 and 1062). This substance, on hydrolysis, yields ψ -opianic acid and ω -aminoethylpiperonylcarboxylic anhydride, and conversely it may be synthesised by simply heating ψ -opianic acid and ω -aminoethylpiperonylcarboxylic anhydride at 180° . When this experiment was described (*loc. cit.*, p. 1079), this important synthesis was assumed to take place according to the equation:



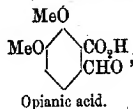
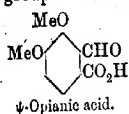
and it was suggested (p. 1002) that the constitution of *berberal* must be represented thus:



The formula for berberine itself, given at the commencement of this section, was largely based on this constitutional formula for *berberal*. ψ -Opianic acid was first obtained as the result of these experiments on the oxidation of berberine, and, as it is difficult to prepare in any quantity by this process, and no other method of preparation has yet been discovered, the mechanism of its condensation with basic substances has not been investigated in detail.

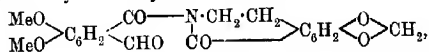
If, however, the formulae of ψ -opianic acid is compared with that of opianic acid, it will be seen that they are both α -aldehydo-

acids, and differ only in the positions of these groups relative to the methoxy-groups:

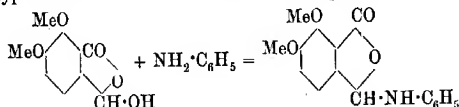


and as this is the only difference in constitution, it may be safely assumed that they will behave in an exactly similar manner when taking part in reactions characteristic of o-aldehyde-acids.

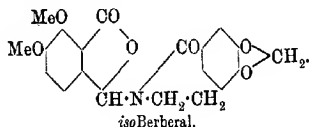
Important evidence in support of this view has already been obtained, since it was shown in the earlier papers (Trans., 1890, 57, 1081) that opianic acid condenses with ω -aminoethylpiperonyl carboxylic anhydride to yield a substance:



which has properties exactly similar to those of berberal, and was therefore named *isoberberal*. During recent years opianic acid has been the subject of detailed investigation, and the results which have been obtained necessitate a modification of our views as to the constitution of *isoberberal*, and consequently of berberal and of berberine itself. Liebermann (*Ber.*, 1886, 19, 2284; 1896, 29, 175) has shown that opianic acid reacts with aniline in the cold to yield anilino-opianic acid, and expressed the opinion that, during this process, the opianic acid reacts as a derivative of hydroxyphthalide in accordance with the equation:

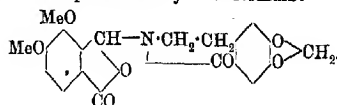


and from the study of this and many other similar condensations, it is clear that, in condensations of opianic acid with basic substances, it is always the carbon atom of the aldehyde group which is attached to the nitrogen atom in the final product. There can be little doubt that a similar process takes place when opianic acid reacts with ω -aminoethylpiperonylcarboxylic anhydride to yield *isoberberal*, and the constitution of this substance is therefore not that originally assigned to it (p. 319), but must be modified to:



Furthermore, since ψ -opianic acid is so exactly similarly constituted to opianic acid, and exhibits in all its reactions so close an analogy with this acid, it cannot be doubted that, when it condenses with basic substances, it also reacts in a similar manner.

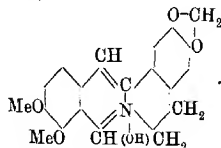
It follows, therefore, that in the formation of berberal by the condensation of ψ -opianic acid with ω -aminoethylpiperonylcarboxylic anhydride, the aldehydic carbon atom of the ψ -opianic acid becomes combined with the nitrogen atom, and the constitution of berberal must therefore be represented by the formula:



Berberal.

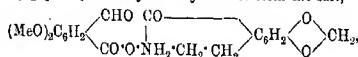
and not by that originally assigned to it (p. 319).*

This new expression is in complete agreement with the properties of berberal, and its acceptance involves the alteration of the position of the methoxy-groups in the old berberine formula (p. 318), so that the constitution of the alkaloid must now be written (compare p. 319):

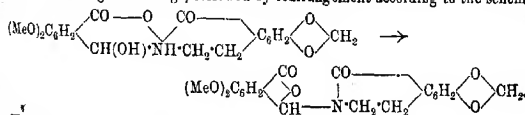


Berberine.

* The actual mechanism of the condensation of opianic acid or ψ -opianic acid with basic substances is probably not so simple as that suggested by Liebermann (*loc. cit.*). When the syntheses of berberal and isoberberal were described (Trans., 1890, 57, 1080 and 1082), it was proved that in both cases the first step is the formation of the salt of the acid with the base. Thus, for example, ψ -opianic acid combines with ω -aminoethylpiperonylcarboxylic anhydride to form the salt,

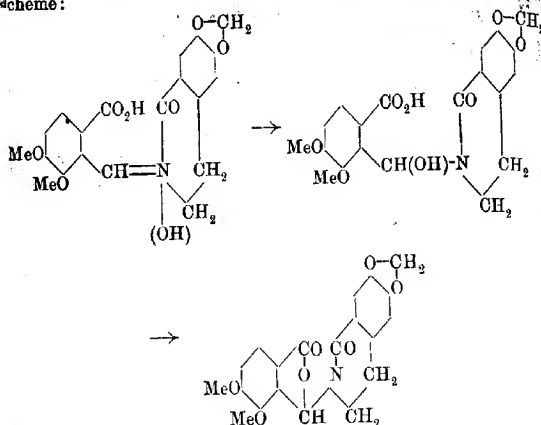


which, when heated at 180°, yields berberal. Most probably aldol formation first takes place during this change, followed by rearrangement according to the scheme:

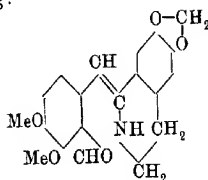


The synthesis of isoberberal takes place in an exactly similar manner, and it is very probable that all such condensations between opianic acid or ψ -opianic acid and basic substances proceed on similar lines.

The formation of berberal by the oxidation of berberine is now easy to understand, and evidently takes place according to the scheme:



The salts of berberine are derived from the hydroxyl formula given above (compare J. Gadamer, *Arch. Pharm.*, 1905, 243, 31), but there is reason to believe that the alkaloid itself exists in the corresponding aldehyde modification. Gadamer (*Chem. Zeit.*, 1902, 26, 291) has shown that, when berberine sulphate is treated with barium hydroxide, it yields a brownish-red, strongly alkaline solution, which doubtless contains the hydroxy-modification of berberine. If, however, this solution is mixed with excess of sodium hydroxide, a yellow modification of berberine is obtained, which apparently has the properties of an aldehyde, and Gadamer has named this modification *berberinal*. The constitution of this modification, based on the new formula for berberine which we have proposed, will be the following:

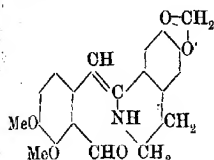


Berberinal.

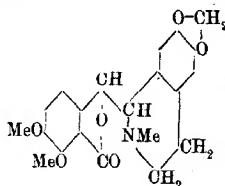
Berberinal yields an oxime, reacts with magnesium alkyl iodides with formation of homologues of berberine (Freund and Beck, *Ber.*,

1904, 37, 3335, and 1905, 38, 1471, and 1472, and treated with a large excess of alkali, is reduced to dihydroberberine and simultaneously oxidised to hydroxyberberine, the aldehyde grouping being converted into $\text{-CH}_2(\text{OH})$ and $\text{-CO}_2\text{H}$ in the manner characteristic of aromatic aldehydes.

The proposed modification of the positions of the methoxy-groups in the berberine formula receives further confirmation from the consideration that berberine occurs along with hydrastine in *hydrastis canadensis*, and the close relationship between these alkaloids becomes very striking if the new formula for berberinal is placed by the side of that of hydrastine:



Berberinal.



Hydrastine.

These alkaloids are, indeed, so closely related as to suggest that hydrastine is either formed in the plant from berberine, or that they are both derived from some common parent.

THE UNIVERSITY,
MANCHESTER.

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

	PAGE
XXXIV.—Decomposition of Dimercurammonium Nitrite by Heat. By PRAFULLA CHANDRA RAY and ATUL CHANDRA GHOSH	323
XXXV.—The Double Nitrites of Mercury and the Metals of the Alkaline Earths. By PRAFULLA CHANDRA RAY	326
XXXVI.—The Constitution of the Amidines. A New Method for Determining Molecular Symmetry. By JULIUS BEREND COHEN and JOSEPH MARSHALL	328
XXXVII.—Silver Amalgams. By HENRY CHAPMAN JONES	336
XXXVIII.—Halogen Derivatives of Malonanilide, Ethyl Malonanilate, and Malonanilic Acid. By FREDERICK DANIEL CHATTAWAY and FREDERICK ALFRED MASON	339
XXXIX.—Reactivity of the Halogens in Organic Compounds. Part IV. Interaction of Bromoacetic, α -Bromopropionic, and α -Bromobutyric Acids and their Sodium Salts with Silver Salts in Aqueous Solution. Catalytic Action of Silver Halides. By GEORGE SENTER	346
XL.—Derivatives of <i>S</i> -Phenylphenazothionium. Part III. By EDWARD DE BARRY BARNETT and SAMUEL SMILES	362
XLI.—Apparatus for Demonstrating the Electrolysis of Hydrochloric Acid. By AUGUSTUS EDWARD DIXON and JOHN TAYLOR	374
LII.—The Solubility of Potassium Sulphate in Concentrated Aqueous Solutions of Non-Electrolytes. By JOHN JACOB FOX and ARTHUR JOSIAH HOFFMEISTER GAUGE	377
LIII.—The Action of Calcium and Lithium on Organic Halides. By JAMES FREDERICK SPENCER and GWYNNEEDD MARY PRICE	385
LIV.—The Influence of Radium Emanation on Equilibrium in a Gaseous System. By FRANCIS LAWRY USHER	389
LV.—Attempted Resolution of Racemic Aldehydes. By WILLIAM ORD WOOTTON	405
LVI.—The Relation between Reactivity and Chemical Constitution of Certain Halogen Compounds. By HANS THACHER CLARKE	416
LVII.—The Vapour Pressures of Two Perfectly Miscible Solids and their Solid Solutions. By ERNEST VANSTONE, B.Sc. (Wales) (1851 Exhibition Research Scholar University College, Cardiff, formerly "Isaac Roberts" Research Scholar)	429

- XLVIII.—Salts and Ethers of 2,3,5-Trinitro-4-Acetylamino-phenol. By RAPHAEL MERDOLA, F.R.S., and HAROLD KUNTZEN
- XLIX.—Triphenyl-2-pyrone. By SIEGFRIED RUHEMANN
- L.—Diketodiphenylpyrroline and its Analogues. Part III. By SIEGFRIED RUHEMANN
- LI.—The Constitution of Carpaine. Part I. By GEORGE BARGER
- LII.—Optically Active Glycols Derived from *l*-Benzoin and from Methyl *l*-Mandelate. By ALEX. MCKENZIE and HENRY WREN
- LIII.—The Synthesis of Δ^1 -cycloPenteneacetic Acid and 1-Methyl- Δ^2 -cyclohexene-3-acetic Acid. By VICTOR JOHN HARDING and WALTER NORMAN HAWORTH
- LIV.—The Direct Union of Carbon and Hydrogen at High Temperatures. Part II. By JOHN NORMAN PRING
- LV.—The Colour and Constitution of Azo-compounds. Part V. By JOHN THEODORE HEWITT and FERDINAND BERNARD THOLE
- LVI.—Action of Ethyl Cyanoacetate on 5-Chloro-1:1-dimethyl- Δ^4 -cyclohexen-3-one. By ARTHUR WILLIAM CROSSLEY and CHARLES GILLING (Salters' Fellow)
- LVII.—The Influence of Colloids and Fine Suspensions on the Solubility of Gases in Water. Part I. Solubility of Carbon Dioxide and Nitrous Oxide. By ALEXANDER FINDLAY and HENRY JERMAIN MAUDE CREIGHTON, M.A., M.Sc. (1851 Exhibition Science Scholar of Dalhousie University, Halifax, Nova Scotia)
- LVIII.—Absorption Spectra and Melting-point Curves of Aromatic Diazoamines. By CLARENCE SMITH and CONSTANCE HAMILTON WATTS
- LIX.—The Relation between Absorption Spectra and Chemical Constitution. Part XIV. The Aromatic Nitro-compounds and the Quinonoid Theory. By EDWARD CHARLES CYRIL BALY, WILLIAM BRADSHAW TUCK, and EFFIE GWENDOLINE MARSDEN
- LX.—The Isolation of Stable Salt Hydrates, with Special Reference to the Stable Hydrates of Sodium Carbonate. By ALEXANDER CHARLES CUMMING
- LXI.—Affinity Relations of Cupric Oxide and of Cupric Hydroxide. By ARTHUR JOHN ALLMAND
- LXII.—Solubilities Below and Above the Critical Temperature. By DAN TYLER
- LXIII.—A Supposed Case of Stereoisomeric Tervalent Nitrogen Compounds. By HUMPHREY OWEN JONES and EDWARD JOHN WHITE
- LXIV.—The Absorption Spectra of *p*-Toluidine, *m*-Xylidine, and of their Condensation Products with Acetaldehyde. By JOHN EDWARD PURVIS

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS:—

PART I.

Organic Chemistry.

	PAGE
LIPPMANN (EDUARD). Oxidation of Unsaturated Compounds by means of Organic Peroxides	i, 149
GUBERNET (MARCEL). Condensation of <i>sec</i> -Butyl Alcohol with its Sodium Derivative	i, 149
LENGEAU (ROBERT). Methylacetenylcarbinol [Butinene- γ -ol]	i, 149
MATHES (HERMANN) and W. HEINTZ. Unsaponifiable Constituents of Japan Tallow	i, 149
FUCHINA (Mlle. CÉCILIE). Dimethyldiethyldicarbinol [γ -Dimethylhexane- γ -diol]	i, 150
SEIBENROCK (E. VON). Drying of Moist Ether	i, 150
HOLMBERG (BROR). Action of Sulphur and Ammonia on Organic Sulphides and Disulphides	i, 150
KARANDÉEFF (B.). Crystalline Form and Optical Characters of Lead Formate	i, 151
KÄUFER (FELIX). [Electrolysis of Carboxy-acids]	i, 151
KÖTZ (ARTHUR). Formation of Dichloroacetic Acid from Trichloroacetaldehyde by Wallach's Method	i, 151
BOESEKEN (JACOB). Catalytic Phenomena	i, 152
SPRING (WALTHER). Detergent Action of Soap Solutions. III. IV.	i, 153
RACC (MANFRED). Xanthic Acid and Dixanthogen [Ethyl Di-oxythiocarbonate]. II.	i, 154
ESCHREIDER (RUDOLF) and ERNST SPÄTH. Addition of Acid Anhydrides to Aldehydes and Ketones	i, 155
BERTRAND (GABRIEL) and GUSTAVE WEISWEILLER. Vicianose, a New Reducing Sugar Containing C_{11}	i, 156
APSCHNITKOFF (ALEXIS V.). Theory of the Nitration of Cellulose	i, 156
MARTARDI (ANGELO). Synthesis of the Phospho-organic Acid of the Seeds of Plants (Posternak's Anhydroxymethylene-diphosphoric Acid)	i, 157
NEUBERG (CARL) and H. POLLAK. Phosphoric Acid Esters of Carbohydrates. I. On Sucrose-phosphoric Acid	i, 157
BOHN (S.) and FRANZ EISSLER. Lipoproteins and the meaning of Fatty Degeneration in Cells. V. Further Syntheses of Lipopeptides. VI. Further Researches on the Cleavage of Lipopeptides	i, 157
ANSCHÜTZ (RICHARD). A New Method of Forming α -Cyanates (Carbimides) and Hofmann's Thiocarbimide Reaction. II.	i, 158
WELICESCU (WILHELM) and HEINRICH ELVERT. Ethyl Oxalosuccinonitrile and Diethyl Dioxalosuccinonitrile	i, 158
MOORE (CHARLES) and J. CH. BONGRAND. Carbon Subnitride, C_2N_2	i, 159
ESGLER (CARL) and O. RUTALA. Naphthene Formation. IV. Formation of Naphthene from Olefines and from Artificial Lubricating Oil and the Synthesis of the Latter	i, 160
ESGLER (CARL) and B. HALMAL. Naphthene Formation. V. The Products of Heating Cylinder Oil Under Pressure	i, 160
ESGLER (CARL). Naphthene Formation. VI. Possible Formation of Hydrocarbons in Nature, and the Origin of the Optical Activity of Petroleum	i, 160
OSTROMISSENSKY (IWAN). Relation between Colour and Constitution	i, 161

- RUPE (HANS) and J. BÜRGIN. Hydrocarbons from Cinnamyl Chloride, $\text{CHPh:CH}\cdot\text{CH}_2\text{Cl}$
- TRÖGER (JULIUS) and E. LUX. Mobility of the Hydrogen Atoms of the Methylene Group in Compounds of the General Formula $\text{R}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CN}$, $\text{R}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, $\text{R}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$
- YXON (PAUL). Aniline Antimonyl Tartrate
- KABLEKOFF (IWAN A.) and AL. SACHANOFF. Complex Compounds of Aluminium Bromide with Organic Compounds
- DEUTSCHE GOLD- & SILBER-SCHNEID-ANSTALT. Preparation of Sodium Arylimides
- CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERRING. Preparation of Cerium Phenoxides
- HINSBERG (OSCAR). Behaviour of Phenyl Sulphide towards Hydrogen Peroxide
- HOLMBERG (BROR). *p*-Tolyl Trisulphide
- SCHMIDT (JULIUS) and HERMANN LUMPP. Phenanthrene Series. XXVI. Conversion of 9-Chloro-10-hydroxyphenanthrene into other Phenanthrene Derivatives
- HOFFMANN (F.), LA ROCHE & Co. Preparation of Carbonatoguaiacol-sulphonic Acid and its Salts
- MANNICH (CARL) and W. JACOBSON. Hydroxyphenylalkylamines and Dihydroxyphenylalkylamines
- HOFFMANN (KARL A.), HEINZ KIRMREUTHER, and A. THAL. Quinocarbonium Perchlorates (II) and the Solvent Action of Chlorinated Ethanes
- SCHURBAKOVSKY (K.). Action of α -Bromonaphthalene and Magnesium on Certain Carbonyl Compounds
- REID (E. EMMET). Preparation of Nitriles
- HOUBEN (JOSEF) and WALTER BRASSERT. Action of Alcoholic Hydrogen Chloride on *m*-Methylnitrosoaminobenzoic Acid
- EINHORN (ALFRED). New Drugs. V.
- EINHORN (ALFRED) and EMIL UHLFELDER. Diethylaminoethyl and Piperidinoethyl *p*-Aminobenzoates
- EINHORN (ALFRED), KARL FIEDLER, CARL LADISCH, and EMIL UHLFELDER. Alkylaminoalkyl *p*-Aminobenzoates
- EINHORN (ALFRED) and EMIL UHLFELDER. Esters and Alkylamino-esters of 3:4-Diaminobenzoic Acid
- ANSELMINO (OTTO). Isomerism of Anils (Schiff's Bases)
- RIIBER (C. N.) and V. MORITZ GOLDSCHMIDT. Differences between Cinnamic Acid from Storax and Synthetical Cinnamic Acid
- LIEBERMANN (CARL) and H. TRUCKSÄSS. Transformations of *allo*-Cinnamic and *iso*-Cinnamic Acids
- ERLENMEYER (EMIL). Mechanism of the Transformation of α -Hydroxy- β -unsaturated Acids into the Isomeric γ -Keto-acids
- ANILINFARBEN- & EXTRAKT-FABRIKEN VORM. J. R. GRIGY. [Preparation of Triphenylmethane Colouring Matters from Diortho-substitute Benzaldehydes]
- FRIEDLÄNDER (PAUL). *p*-Methoxysalicylaldehyde
- NORLTING (FRANCIS A. M.). Orthovanillin [2-Hydroxy-3-methoxybenzaldehyde] and its Derivatives
- PETRENKO-KRITSCHENKO (PAVEL IW.). Carbonyl Group in the Nascent State
- JACKSON (C. LORINC) and H. A. FLINT. Tetrabromodiketocyclopentene
- BORSCHÉ (WALTHER). Nitrosation of the Simplest Cyclic Ketones
- SENDERENS (JEAN B.). Catalytic Preparation of Aromatic Ketones
- METER (KURT H.). Additive Compounds of Ketones and Quinones with Acids and Phenols
- GILDEMEISTER (EDUARD) and HUGO KÖHLER. Occurrence of β -Pinene and β -Pinocamphone in Hyssop Oil, and Some Observations on Isomerides in the Pinene Series

CONTENTS.

v

	PAGE
SEMMER (FRIEDRICH W.J.). Constituents of Ethereal Oils. Tetrahydro-santalene, $C_{20}H_{32}$	i, 181
STUCHENKO (P.). Action of Magnesium and Allyl Bromide on Menthone	i, 181
CUSMANSO (GUIDO). Behaviour of Alicyclic Hydroxylamines and Hydroxyl-amineoximes towards Nitrous Acid. I.	i, 182
WHITTELSEY (THEODOR). New Occurrence of <i>l</i> -Camphor	i, 184
WALBAUM (HEINRICH) and WILHELM MÜLLER. Coriander Oils	i, 184
ROCHE-BERTRAND FILS [with JUSTIN DUPONT and LOUIS LABAUNE, and J. LEROIDE]. [Essential Oils]	i, 184
GILDEMEISTER (EDUARD) and WILHELM MÜLLER. Constituents of Oil of Lemon	i, 185
LEINBACH (ROBERT). Essential Oil from the Seeds of <i>Monodora grandifolia</i>	i, 186
FRIED (KARL) and W. PFAFFENDORFF. A Condensation Product of Camphorone and its Conversion into Oxindirubin	i, 186
HOFMANN (KARL A.), A. METZLER, and H. LECHER. Oxonium Perchlorates	i, 187
FOA (IDA). New Selenium Compound	i, 187
REICHARD (G.). Production of a Volatile Aromatic Substance from Solutions of Morphine Salts	i, 187
DITTLH (H.). Partial Racemism	i, 188
MARCHLEWSKI (LEON). Hemipyttol	i, 188
GRÜSNER DE CONINCK (WILLIAM). Pyridine Hydrate	i, 188
PETRENKO-KRITSCHENKO (PAVEL Iw.) and JOH. SCHÖTTLE. Condensation of Esters of Acetonedicarboxylic Acid with Aldehydes by means of Ammonia and Amines. VI. Tautomerism of Ethyl 2:6-Diphenyl-4-pyridone-3:5-dicarboxylate	i, 188
RAMBERGER (EUGEN) and SVEN LINDBERG. Anthranil. XVI. Relation of Anthrocanic Acid (2-Anthranilcarboxylic Acid) to Anthranil	i, 189
BOESCH (WALTHER). Cinchonic Acid Syntheses	i, 189
BRUN (JULIUS VON). Elimination of Alkyl Radicles and Fission of Organic Bases by means of Cyanogen Bromide and Phosphorus Halides	i, 189
BEZDIK (A.) and PAUL FRIEDLÄNDER. Indigoid Dyes. V. Indigoid Dyes of the Anthracene Series	i, 189
GABRIEL (SIEGMUND). Synthesis of Oxazoles and Thiazoles. I.	i, 190
FRECHES (GUSTAV) and PAUL FÖRSTER. Action of Hydrazines on Thiocyanosacetic Acid and its Ethyl Ester	i, 190
FOZZIO (GIACOMO). Case of Isomerism. [Acylazoaryl Compounds]	i, 192
FOZZIO (GIACOMO) and R. GIOVETTI. Passage of the Nitro-group from an Aliphatic Carbon Atom to the Benzene Nucleus	i, 194
CIVRA (ROBERTO) and MAURICE PADOA. Limiting Cases between Polymorphism and Isomerism	i, 196
HANTZSCH (ARTHUR) and ROBERT ROBINSON. Pantachromism of Dimethyl- and Diphenyl-violurates	i, 196
HANTZSCH (ARTHUR) and J. HEILBRON. Pantachromic Salts of Oximino-oxazolones	i, 198
HANTZSCH (ARTHUR). Pantachromism of Violurates and Salts of Analogous Oximino-ketones	i, 200
HANTZSCH (ARTHUR) and ROBERT ROBINSON. Purpuric Acid	i, 200
DEBREIT (ERWIN). Synthesis of 5:7:5':7'-Tetrachloroindigotin	i, 201
VOSEKLOCHTEN (EDUARD) and L. KRANTZ. Quinoline-Red	i, 201
ULMANN (FRITZ) and ERWIN CASSIRER. Acenaphthene Series	i, 201
LANDAUER (PAUL) and HUGO WEIL. Methylene-Blue	i, 202
BELOW (CARL) and KARL HAAS. Synthesis of Hetero-condensed Heterocyclic Compounds with Two Nuclei. Derivatives of 2-Methyl-1:3-triazo-7:0'-pyrimidine [2-Methyl-1:3:7:9-benzotetrazole] from 5-Amino-2-methyl-1:3:4-triazole	i, 203
HANTZSCH (ARTHUR) and PHILIP W. ROBERTSON. Yellow and Red Forms of Salts and Hydrates of Hydroxyazo-derivatives	i, 203

	PAGE
BÖLOW (CARL) and C. BOZENTHARDT. Formation and Decomposition of Symmetrical Bisazo-compounds of Ethyl Arylhydrazonesoxalylbis-hydrazonoacetates and of Ethyl Malonylbishydrazonoacetate	i, 205
MARCHLEWSKI (LEON) and J. ROEHL. Azo-dyes derived from 2:4-Dimethylpyrrole and Hemopyrrole	i, 208
NOMBLOT (LOUIS). Reduction of Nitroso-derivatives of Acetyl- and Benzoyl-hydrazobenzene	i, 208
GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL. [Preparation of <i>p</i> -Aminophenyl-2-azimino-5-naphthol-7-sulphonic Acid]	i, 208
TRÖGER (JULIUS) and A. WESTERKAMP. Azoxyhydrazinesulphonic Acids	i, 207
BILTZ (WILHELM) and HANS STRINER. The Adsorption of Proteins	i, 203
GUPTA (NOCENDRAMOHON). Composition of the Products of the Alkaline Hydrolysis of Crystalline Egg-Albumin	i, 209
MEYER (GUSTAVE M.). The Preparation and Properties of Iodo-Mucoids	i, 207
ROAF (HERBERT E.). The Relation of Proteins to Crystalloids. I. The Osmotic Pressure of Hemoglobin and the Laking of Red Blood-corpuscles	i, 209
KÜSTER (WILLIAM). Blood Colouring Matter	i, 210
SADIKOFF (WL. S.). Behaviour of Gelatinous Substances or Collains towards Carbon Disulphide	i, 211
ABDERHAIDEN (EMIL). The Scission Products Resulting from the Partial Hydrolysis of Proteins	i, 211
MEYER (KURT). Trypsin and Antitrypsin	i, 211
HOLDERER (MAURICE). Influence of the Reaction of the Medium on the Filtration of Diastases	i, 212
HOLDERER (MAURICE). Influence of the Reaction of the Medium on the Filtration of Malt Enzymes	i, 212
BERTRAND (GARRIEL) and MAURICE HOLDERER. Cellase and the Diastatic Decomposition of Cellose	i, 212

PART II.

General and Physical Chemistry.

AUREL (EDMOND VAN). Pulfrich's Ratio between Volume Contraction and Refractive Power of Liquid Mixtures	ii, 169
HANTZSCH (ARTHUR) and KURT MEISENBURG. Molecular Refraction of Isomerisable Unsaturated Acids and their Salts	ii, 169
NATANSON (LADISLAS). Theory of Dispersion in Gaseous Substances	ii, 170
FIEBIG (PAUL). The Long-waved Portion of the Spectrum of Titanium	ii, 170
ZICKENDRAHT (HANS). Investigation of the Sodium Spectra	ii, 171
HOFMANN (KARL A.) and HRNZ KIRNREUTHER. Spectra of the Erbium Compounds and Stark's Valency Hypothesis	ii, 171
HEMSLEIGH (GUSTAVE A.) and CHARLES DE WATTEVILLE. Flame Spectrum of Iron at a High Temperature	ii, 172
RUBENS (HEINRICH) and H. HOLMAGEL. Measurements in the Long-waved Spectrum	ii, 172
JONES (HARRY C.) and W. W. STRONG. Absorption Spectra of Various Salts in Solution and the Effect of Temperature on Such Spectra	ii, 172
GERNEZ (DÉSIRÉ). Restoration of Phosphorescence to Sulphides of the Alkaline Earths	ii, 173
COHEN (ALFRED) and HANS BECKER. Photochemical Equilibria. III. Photochemical Equilibrium of Carbonyl Chloride	ii, 173

CONTENTS.

vii

	PAGE
WRIGHT (FRITZ). Chemical Action of Light. V. Photochemical Phenomena in Dye Solutions	ii, 174
BROCHET (ANDRÉ). Radioactivity of some Waste Springs in the Vosges	ii, 174
CHAUDIER (J.) and KDOUARD CHAUVENET. Radioactivity of Halogen and Oxyhalogen Compounds of Thorium	ii, 174
BUTTERFORD (ERNEST). The Action of the α -Rays on Glass	ii, 175
WILSON (W.). The Absorption Law of β -Rays	ii, 175
BUTTERFORD (ERNEST) and BERTRAM B. BOLTWOOD. Production of Helium by Radium	ii, 175
STRETT (ROBERT J.). The Accumulation of Helium in Geological Time. III.	ii, 175
POOLE (HORACE H.). Rate of Evolution of Heat by Pitchblende	ii, 176
HORTON (FRANK). The Emission of Positive Rays from Heated Phosphorus Compounds	ii, 176
SEEROFF (S. W.). Electrical Conductivity and Constitution of Dissolved Substances	ii, 177
McBAIN (JAMES W.) and MILLICENT TAYLOR. Electrical Conductivity of Soap Solutions	ii, 177
FÄRI (WALTER). Diminution of Conductivity by Colloids and Observations relating to the Conductivity of Serum	ii, 177
BECTY (EDMOND). Dielectric Cohesion of Neon	ii, 178
CHEN (ERNST) and HUGO R. KRUYT. Thermodynamics of Standard Cells	ii, 178
LAFORET (F.) and P. DE LA GORCE. Electrochemical Equivalent of Silver	ii, 178
DEYSTER (CHARLES M. VAN) and H. J. VAN LUMMEN. Correction for the Method of Determining Galvanic Ennobling of Metals	ii, 179
LOREZ (RICHARD). Electrolysis of Molten Salts	ii, 179
HESSLER (FRIEDRICH). Magnetisable Alloys of Manganese	ii, 179
FESKE (WILHELM). Magnetic Measurements of Platinum Metals and of Monoclinic Crystals, in Particular of Iron, Cobalt, and Nickel Salts	ii, 179
PASCAL (PAUL). Use of the Magnetic Field as a means of Determining Constitution in Organic Chemistry. IV.	ii, 179
SIDDY (FREDERICK) and ARTHUR J. BERRY. Conduction of Heat through Rarefied Gases	ii, 180
SCHIFFER (HERMANN). Heat Capacity of Certain Metals and Compounds of Metals	ii, 181
SAPROSHNIKOFF (ALEXIS V.). Specific Heat of Metallic Alloys	ii, 182
SVLTZENBERG (H.). Melting-Point Determinations at Low Temperatures	ii, 182
MEYER (JULIUS). Measurement of the Heats of Liquefaction of Acetic Acid, Benzene, and Nitrobenzene	ii, 182
MAMELI (EFISIO). Chloroacetic Acid as a Cryoscopic Solvent	ii, 182
HABN (ALEXANDER). A New Fractionating Column	ii, 183
MAIER (RUDOLF). An Apparatus for the Measurement of the Vapour Pressures of Dilute Aqueous Solutions	ii, 183
STOTT (WILLIAM E.). Partial Pressures of Liquid Mixtures	ii, 184
DOLEZALEK (FRIEDRICH). Binary Mixtures and Concentrated Solutions. II.	ii, 184
BARKER (JONATHAN T.). Experimental Determination and Thermodynamic Calculation of the Vapour Pressures of Toluene, Naphthalene, and Benzene	ii, 185
MEYER (KIRSWINE) and BJERRUM. Corresponding States	ii, 186
VAILLANT (PIERRE). Laws of Evaporation	ii, 186
SVETOSLAVSKI (SVETOSLAVSKY) (W.). Thermochemical Investigations of Organic Compounds. IV—VII. Sulphur, Halogen, and Unsaturated Compounds	ii, 187
KNOTT (C. G.). Andrews' Measurements of the Compression of Carbon Dioxide and of Mixtures of Carbon Dioxide and Nitrogen	ii, 187
FRÖTZ (LUDWIG). Dependence of the Cubic Compressibility of Potassium and Sodium on the Temperature	ii, 187
CAMPBELL (FRANK K.) and WILLIAM O. ROBINSON. Condensation of Water by Electrolytes	ii, 188
RAVSKINE (A. O.). A Method of Determining the Viscosity of Gases, especially those available only in Small Quantities	ii, 188

	PAGE
FAUST (O.) and GUSTAV TAMMANN. Torsional Elasticity and its Connexion with Viscosity	ii, 189
RUSSENBERGER (J. H.). Absorption of Liquids by Porous Substances	ii, 189
LEOPOLD (GERARD H.). Three-phase Equilibrium (with a Pressure Minimum) of a Dissociating Compound of Two Components. III.	ii, 190
TERESCHIN (S.). Relation between Density and Degree of Dissociation of Aqueous Salt Solutions	ii, 190
SKRATUP (ZDENKO H.). Behaviour of Aqueous Solutions in Capillary Actions	ii, 191
THOVERT (J.). Diffusion and the Kinetic Theory of Solutions	ii, 191
BECHHOLD (HEINRICH) and J. ZIEGLER. Action of Membranes	ii, 191
SCHÜKAREFF (A. N.). Properties of Solutions at their Critical Solution-Temperatures	ii, 192
HERZ (WALTER). An Example of Solubility Influence	ii, 192
GAILLARD (GASTON). Difference in the Speed of Dissolution of Sucrose Crystals at their Different Faces	ii, 193
RINNE (FRITZ). Crystallisation in Fused Masses, owing to the Liberation of Gas	ii, 193
FOUQUET (G.). Spontaneous Crystallisation of Sugar	ii, 193
LEHMANN (OTTO). Liquid Crystals and Avogadro's Hypothesis	ii, 193
LEHMANN (OTTO). Self-purification of Liquid Crystals	ii, 194
OSTWALD (W.A.). Emulsions	ii, 194
RUER (RUDOLF). Independent Components and Compounds	ii, 194
SMITS (ANDREAS). Allotropy and Internal Equilibrium	ii, 195
KRUYT (HUGO R.). The Equilibrium Solid-Liquid-Gas in Binary Systems which Present Mixed Crystals	ii, 195
SCHREINEMAKERS (FRANS A. H.). Equilibria in Quaternary Systems. The System: Lithium Sulphate-Ammonium Sulphate-Ferrous Sulphate and Water	ii, 195
BÖTTGER (WILHELM). Criteria for the Determination of the Sensitiveness of Precipitation Reactions	ii, 195
MICHAEL (ARTHUR). Relationship between the Structure of the Aliphatic Alcohols and their Rate of Esterification	ii, 196
PERRÉDES (P. É. F.). Modification of Dunstan and Short's Extraction Apparatus	ii, 196
GRASSI (UGO). [Lecture] Experiments in Physical Chemistry	ii, 196

Inorganic Chemistry.

HOFFMANN (MAX K.). Formulation and Nomenclature of Inorganic Compounds	ii, 196
LOMBARD (MAURICE). Chemical and Biological Effects of Ultra-violet Light	ii, 197
COPPADORO (ANGELO). Utilisation of Electrolytic Chlorine for the Simultaneous Production of Hydrochloric and Sulphuric Acids	ii, 197
BOHR (CHRISTIAN). Solubility of Gases in Concentrated Sulphuric Acid and in Mixtures of Sulphuric Acid and Water	ii, 198
EPHRAIM (FRITZ) and M. GUREWITSCH. Amides of Sulphuric Acid	ii, 198
COHEN (ERNST) and J. F. KRÖNER. Allotropy of Tellurium	ii, 199
ADWENTOWSKI (KAROL). Behaviour of Nitric Oxide at Low Temperatures	ii, 199
SAPOSHNIKOFF (ALEXIS V.). Molecular Weight of Nitrous Acid in Aqueous Solution	ii, 200
STOCK (ALFRED) (with MAX RUDOLPH). Compounds of Sulphur and Phosphorus. V. Tetraphosphorus Trisulphide, P_4S_3	ii, 200
STOCK (ALFRED) [with BERLA HERSCOVICI]. Compounds of Sulphur and Phosphorus. VI. Tetraphosphorus Heptasulphide, P_4S_7	ii, 201
BILTZ (HEINRICH). Crystalline Boron. II.	ii, 201

CONTENTS.

ix

	PAGE
CAMBOULIVES (PIERRE). Action of Carbon Tetrachloride Vapour on Anhydrides and Oxides	ii, 202
CAMBOULIVES (PIERRE). Action of Carbon Tetrachloride Vapour on Minerals	ii, 202
ESSTEIN (FRIEDRICH) and P. KRASSA. Conductivity of the Inner Cone of Divided Flames. The Explosibility of Gaseous Mixtures	ii, 202
TANATAR (SEBASTIAN). Existence of Real Percarbonates and their Differentiation from Carbonates with Hydrogen Peroxide of Crystallisation	ii, 203
WILKE-DÖRFERT (ERNST). So-called Amorphous Silicon	ii, 204
SCHWENTSCHUSCHNY (S. F.) and F. RAMBACH. Alloys of the Chlorides of the Alkali Metals	ii, 204
EFFHAIM (FRITZ) and ETTA MAJLER. Some Thiophosphates	ii, 206
EFFHAIM (FRITZ) and ETTA MAJLER. Selenophosphates	ii, 206
EFFHAIM (FRITZ) and MAX BRAND. Lithium Phosphomolybdates	ii, 207
EFFHAIM (FRITZ) and HEINRICH HERSCHFINKEL. Rubidium and Cesium Phospho- and Arsenomolybdates	ii, 208
WALLACE (ROBERT C.). Dimorphism of Ammonium Haloids	ii, 208
DAS (TARAK NATH). Properties of Precipitated Silver	ii, 209
THORPE (SIR EDWARD) and ARTHUR G. FRANCIS. Atomic Weight of Strontium	ii, 209
SELTATIC (ETTORE). Action of some Salts of Ammonium on the Alkaline Earth Carbonates	ii, 209
DOXY-HENAUULT (OCTAVE). Electrolysis of Cupric Solutions	ii, 209
RASSEFOSSE (ANDRE). Coloration of Salts	ii, 210
NACMANN (ALEXANDER) [with MAX HAMERS and EMIL HENNINGER]. Reactions in Non-Aqueous Solutions. V. In Ethyl Acetate	ii, 211
KORN-ABREST (ÉMILE). Action of Heat on Aluminium in a Vacuum	ii, 212
VEREULI (AUGUSTE). Synthetical Production of Sapphires by Fusion	ii, 212
D'ANS (JOH.). Do Clays and Cements Adsorb CO ₂ Ions?	ii, 213
DEISS (EUGEN). Formation and Properties of Colloidal Manganese Dioxide	ii, 213
SACKUR (OTTO). The Thermal Formation of Manganates. I.	ii, 214
SACKUR (OTTO). The Thermal Formation of Manganates. II. Molecular-Weight Determinations in Fused Alkali Carbonates	ii, 215
CHAPPEY (GEORGES) and S. BONNEROT. Cementation of Iron by Solid Carbon	ii, 215
WEISS (LUDWIG) [with A. MARTIN and A. STIMMELMAYER]. Metallic Tungsten	ii, 216
GIOLITTI (FEDERICO) and O. CECCARELLI. Corrosion of Bronzes in Solutions of Electrolytes	ii, 217
WEISS (LUDWIG) and EUGEN NEUMANN. Metallic Zirconium	ii, 217
WEDEKIND (EDGAR). Natural Zirconium Earths	ii, 218
ZANI (VITO). Physical and Chemical Properties of some Varieties of Antimony Trisulphide	ii, 219

Mineralogical Chemistry.

PALACHE (CHARLES). Mineralogy of Franklin Furnace, New Jersey	ii, 219
SCHALLER (WALDEMAR T.) and FREDERICK L. RANSOME. Bismite	ii, 220
MILLOSEVICH (FEDERICO). Variety of Cobaltiferous Calcite from Capo Calamita, Elba	ii, 221
HAUSER (OTTO). The Plumbonitobite Earths	ii, 221
MARCKWALD (WILLY). A Uranium Ore from German East Africa	ii, 221
DUPARC (LOUIS), R. SABOT, and M. WUNDER. Minerals from the Pegmatites of Madagascar	ii, 221
NASINI (RAFFAELLO), MARIO GIACOMO LEVI, and F. AGENO. Chemo-physical Investigations and Analysis of the Iron- and Arsenic-containing Water of Roncegno	ii, 222

CONTENTS

Physiological Chemistry

	PAGE
MANSFIELD (G.). Narcosis and Want of Oxygen. II. The Effect of Deprivation of Oxygen on the Resting Current of Frog's Skin	ii, 222
WOLFSOHN (J. M.) and L. W. KETRON. Gaseous Metabolism of the Dog's Heart during Vagus Inhibition	ii, 222
MEYERSTEIN (WILHELM). The Inhibition of Soap Hemolysis	ii, 223
SUTHERLAND (W. D.) and DAVID McCAY. Observations on the Inhibitory Influence Exerted by Hypertonic Saline Solutions and Calcium Chloride Solutions on the Action of Specific Hemolysins with Suggestions as to the Therapy of Blackwater Fever.	ii, 223
MARINO-ZUCO (FRANCESCO) and L. GIUGANINO. Action of Biotoxin on Blood.	ii, 223
MENDEL (LAFAYETTE B.) and WARREN W. HILDITCH. Influence of Alcohol on Metabolism.	ii, 223
BALDWIN (WESLEY M.). Relation of Pancreas to Sugar Metabolism.	ii, 224
RIEPPY (H.). Digestion of Inulin	ii, 224
GOLDTHWAITE (NELLIE E.). Effects of Carbohydrates on the Artificial Digestion of Casein.	ii, 224
PENNINGTON (MARY E.). Chemical and Bacteriological Study of Fresh Eggs.	ii, 224
LIPSCHUTZ (ALEXANDER). The Phosphorus-content of Growing Dogs	ii, 224
CUSHNY (ARTHUR R.). Irregularities of the Mammalian Heart under Aconitine	ii, 224
SIMPSON (G. C. E.). Influence of the Pancreas on the Glycolytic Power of Muscle.	ii, 225
SCHULZ (HUGO). The Silicic Acid in Whartonian Jelly.	ii, 225
PFLÜGER (EDUARD) and PETER JUNKERSDOFF. The Parent Substance of Glycogen.	ii, 225
PFLÜGER (EDUARD). The Parent Substance of Glycogen	ii, 225
JUNKERSDOFF (PETER). Influence of Phloridzin on the Sugar in the Blood	ii, 225
PFLÜGER (EDUARD). Estimation of Glycogen in the Tortoise's Liver.	ii, 225
LUCKHARDT (A. B.). Physiology of Lymph. X. The Comparative Electrical Conductivity of Lymph and Serum, and its Bearing on Theories of Lymph Formation	ii, 226
LUSSKY (HERBERT O.). Physiology of Lymph. XI. The Fractional Coagulation of Lymph	ii, 226
SARTHOUS (J.). Presence in Cow's Milk of an Anaerobias and a Catalase.	ii, 226
BORDAS (FRÉD.) and F. TOUPAIN. Reactions of Curdled Milk due to the Colloidal State.	ii, 226
LIPSCHÜTZ (ALEXANDER). The Phosphorus in Faeces.	ii, 227
BAER (JULIUS) and LEON BLUM. The Degradation of Fatty Acids in Diabetes mellitus	ii, 227
NISHI (M.). Formation of Glycogen in the Liver of Tortoises with Pancreatic Diabetes	ii, 227
RINGER (A. I.) and GRAHAM LUSK. The Production of Sugar from Amino-acids.	ii, 227
WOODYATT, R. T. Phloridzin Glycocholia	ii, 227
HENDERSON (YANDÉLL). Acapnia and Shock. V. Failure of Respiration after Intense Pain.	ii, 227
JOSEPH (DON R.) and SAMUEL J. MELTZER. Antagonistic Action of Barium and Magnesium	ii, 228
FRÖHLICH (ALFRED) and OTTO LOEWI. The Increase of Susceptibility to Adrenaline Produced by Cocaine	ii, 228
DAKIN (HENRY D.). Fate of Sodium Benzoate in the Human Organism.	ii, 228
EMBLEY (E. H.). The Action of Ether on the Circulation	ii, 228
MOORE (BENJAMIN), MISS S. C. M. SOWTON, F. W. BAKER-YOUNG, and T. ARTHUR WEBSTER. The Chemistry and Bio-chemical and Physiological Properties of a Sapo-glucoside obtained from the Seeds of <i>Bassia longifolia</i> (Mowrah Seeds)	ii, 228

CONTENTS.

xi

	PAGE
VALET (VICTOR H.) and AUGUSTUS D. WALLER. Comparative Action of Stovaine and Cocaine as Measured by their Direct Effect on the Contractility of Isolated Muscle	ii, 228
SWAIN (ROBERT E.) and W. G. BATEMAN. Toxicity of Thallium Salts	ii, 229
PRUSSAK (MILÉ. GUSTAVA). Mercury and Hirudin	ii, 229
BANG (IVAR). Cobra Poison and Hemolysis. III.	ii, 229

Chemistry of Vegetable Physiology and Agriculture.

LEBEDEFF (A. J.). Assimilation of Carbon by Bacteria which Oxidise Hydrogen	ii, 229
PRINGSHEIM (HANS). Cellulose as Source of Energy in the Assimilation of Atmospheric Nitrogen	ii, 230
PRINGSHEIM (HANS) and ERNST PRINGSHEIM. Agar-Agar as Source of Energy in the Assimilation of Atmospheric Nitrogen	ii, 230
RITTER (G.). Ammonia and Nitrates as Sources of Nitrogen for Mould Fungi TACKER (BRUNO). Production and Utilisation of Nitrous Oxide by Bacteria KING (WALTER E.) and CHARLES J. T. DORTLAND. Influence of Depth of Cultivation on Soil Bacteria and their Activities	ii, 231
KUSSEROW (R.). New Theory of Alcoholic Fermentation	ii, 231
MAURAIN (CHARLES) and G. WACCOLIER. Action of Ultra-violet Light on Wine During Fermentation	ii, 231
THILLAT (AUGUSTE). Causes Favouring the Formation of Acetaldehyde in Wine	ii, 232
RANKIN (ALLAN C.). Germicidal Action of Metals and its Relation to the Production of Peroxide of Hydrogen	ii, 232
THILLAT (AUGUSTE). Disinfection by the Incomplete Combustion of Straw	ii, 232
NICHELS (HENRI). Action of Aqueous Solutions of Electrolytes on Germination	ii, 232
OTTO (RICHARD) and W. D. KOOPER. The Changes Taking Place in the Composition of Fruits which Ripen after being Gathered	ii, 233
CAYAZZA (LUIGI ERMANN). Microchemical and Physiological Studies on Tannin	ii, 233
POLSTORFF (KARL). Choline Content of Certain Edible Fungi	ii, 234
BOURQUELOT (ÉMILE) and MARC BRIDEL. Presence of Gentiopierin in <i>Chlora perfoliata</i>	ii, 234
POLSTORFF (KARL). Occurrence of Betaines and Choline in Drugs containing Caffeine and Theobromine	ii, 234
HAIES (EUGENE). Presence of an Alkaloid in the seeds of <i>Lunaria biennis</i> CIAMICIAN (GIACOMO L.) and CIRO RAVENNA. Formation of Glucosides by means of Plants	ii, 234
RÖHRIG (A.). Occurrence of Formic Acid in Raspberries	ii, 235
CEVALIER (J.). Influence of Cultivation on the Alkaloid-content of Certain <i>Solanaceae</i>	ii, 235
WALBAUM (HEINRICH). Occurrence of Anisyl Alcohol and Anisaldehyde in the Fruit of Tahiti Vanilla	ii, 235
RAVENNA (CIRO) and M. ZAMORANI. Behaviour of Plants towards Lithium Salts	ii, 235
KRAINSKY (A.). Accumulation of Nitrogen in Soils	ii, 236
AGULON (H.). Use of Boron as a Catalytic Manure	ii, 236
MITSCHELICH (EILHARD A.). Manuring with Carbon Dioxide	ii, 236
ERENBERG (PAUL). Actions of Zinc in Pot Experiments. Contribution to the Ammonia Question. II.	ii, 236

Analytical Chemistry.

	PAGE
EMICH (FRIEDRICH). Micro-chemistry with Special Reference to Behrens' Work	ii, 237
HOHMANN (KARL). Automatic Gas Analysis Apparatus	ii, 237
PAAL (CARL) and WILHELM HARTMANN. Gas-volumetric Estimation of Hydrogen by Catalytic Absorption	ii, 237
CHARITSCHKOFF (K. W.). New Reagent for Hydrogen Peroxide	ii, 238
BLEEKER (IRVING B.). The Effect of Continued Grinding on Water of Crystallisation	ii, 238
DAS (TARAK NATH). Estimation of Chlorates in the Presence of Nitrates and Chlorides	ii, 238
PREUSS (GEORGE). Apparatus for the Estimation of Sulphur in Iron and Steel	ii, 238
BENEDICT (STANLEY R.). Estimation of Total Sulphur in Urine	ii, 239
ROUILLARD and GOUJON. Desulphitation of Wine by means of Hexamethylenetetramine	ii, 239
HOLLIGER (M.). Volumetric Estimation of Sulphuric Acid by the Barium Chromate Method	ii, 239
HOWARD (HENRY). The Heat of Chemical Reactions as a Basis for a New Analytical Method	ii, 239
BEEL (ERNST) and A. W. JURRISEN. Gas-volumetric Analysis with the "Decomposition Flask," and the Estimation of Nitrogen in Smokeless Powders	ii, 240
HEUBNER (WOLFGANG) and GEORG WIEGNER. Distilling Apparatus for Nitrogen Estimations by Kjeldahl's Method	ii, 240
WILKIE (JOHN M.). [Modification of] Rouché's Method of Estimating Ammonia	ii, 240
ARTMANN (PAUL) [and R. BRANDIS]. Iodometric Estimation of Phosphoric Acid	ii, 241
AZZARELLO (E.). Estimation of Arsenic in Copper	ii, 241
BERTRAND (GABRIEL) and H. AGULHON. Detection of Minute Quantities of Boron in the Organism and in Complex Mixtures	ii, 241
WEIL (HUGO). Use of Lead Peroxide in Organic Combustions	ii, 242
BEEL (ERNST). Estimation of Carbon, Hydrogen, and Nitrogen in Highly Combustible Liquids	ii, 242
STEPHENSON (H. H.). A Simple Burette for the Estimation of Carbon Dioxide	ii, 242
BEEL (ERNST) and A. W. JURRISEN. Assay of Calcium Carbide, Sodium Amalgam, and Zinc Dust with the "Decomposition Flask"	ii, 242
MCCRUDDEN (FRANCIS H.). Quantitative Separation of Calcium and Magnesium in the Presence of Phosphates and Small Amounts of Iron, Devised especially for the Analysis of Foods, Urine, and Fæces	ii, 243
SORNAY (P. DE). Influence of Manganese on the Estimation of Magnesium in Soils	ii, 243
RUFF (ERWIN). New Volumetric Methods for Titrating Zinc or Lead	ii, 243
FRANK (FRITZ) and KARL BINKNER. Estimation of Cinnabar and Sulphur Auratum in Rubber Wares	ii, 244
FENTON (HENRY J. H.). Reaction of Titanium	ii, 244
CAVAZZA (LUIGI E.). Microchemical Detection of Tannins	ii, 244

INDEX OF AUTHORS' NAMES

IN TRANSACTIONS AND ABSTRACTS

A.

Abderhalden, E., i, 211.
 Adwentowski, K., ii, 199.
 Ageno, F. See R. Nasini.
 Agulhon, H., ii, 235.
 Agulhon, H. See also G. Bertrand.
 Allmand, A. J., TRANS., 603.
 Anilinfarben- & Extrakt-Fabriken
 vorm. J. R. Geigy, i, 175.
 Anschütz, R., i, 153.
 Anselmino, O., i, 174.
 Artmann, P., and R. Brandis,
 ii, 241.
 Aubel, E. van, ii, 169.
 Azzarello, E., ii, 241.

B.

Baer, J., and L. Blum, ii, 227.
 Baker-Young, F. W. See B. Moore.
 Baldwin, W. M., ii, 224.
 Baly, E. C. C., Miss E. G. Marsden,
 and W. B. Tuck, TRANS., 571.
 Bamberger, E., and S. Lindberg,
 i, 189.
 Bang, I., ii, 229.
 Barger, G., TRANS., 466.
 Barker, J. T., ii, 185.
 Barnett, E. de B., and S. Smiles,
 TRANS., 362.
 Bateman, W. G. See R. E. Swain.
 Bechhold, H., and J. Ziegler,
 ii, 191.
 Becker, H. See A. Coehn.
 Benedict, S. R., ii, 239.
 Berl, E., ii, 242.
 Berl, E., and A. W. Jurrissen,
 ii, 240, 242.
 Berry, A. J. See F. Soddy.
 Bertrand, G., and H. Agulhon,
 ii, 241.
 Bertrand, G., and M. Holderer,
 i, 212.
 Bertrand, G., and G. Weisweiler,
 i, 156.

Bezdzik, A., and P. Friedländer,
 i, 189.
 Bierry, H., ii, 224.
 Biltz, H., ii, 201.
 Biltz, W., and H. Steiner, i, 209.
 Birkner, K. See F. Frank.
 Bjerrum. See Kirstine Meyer.
 Blecker, I. B., ii, 238.
 Blum, L. See J. Baer.
 Böseken, J., i, 152.
 Böttger, W., ii, 195.
 Bohr, C., ii, 198.
 Boltwood, B. B. See E. Rutherford.
 Bondi, S., and F. Eissler, i, 157.
 Bongrand, J. C. See C. Moureu.
 Bonnerot, S. See G. Charpy.
 Bordas, F., and F. Touplain, ii, 228.
 Borsche, W., i, 178, 189.
 Bourquelot, E., and M. Bridel,
 ii, 234.
 Bouty, E., ii, 178.
 Bozenhardt, C. See C. Bülow.
 Brand, M. See F. Ephraim.
 Brandis, R. See P. Artmann.
 Brassert, W. See J. Houben.
 Braun, J. von, i, 189.
 Bridel, M. See E. Bourquelot.
 Brochet, A., ii, 174.
 Bülow, C., and C. Bozenhardt,
 i, 205.
 Bülow, C., and K. Haas, i, 203.
 Bürgin, J. See H. Rupe.

C.

Camboulives, P., ii, 202.
 Cameron, F. K., and W. O. Robin-
 son, ii, 185.
 Cassirer, E. See F. Ullmann.
 Cavazza, L. E., ii, 238, 244.
 Ceccarelli, O. See F. Giolitti.
 Charitschkoff, K. W., ii, 238.
 Charpy, G., and S. Bonnerot, ii, 215.
 Chattaway, F. D., and F. A. Mason,
 TRANS., 338.

Chaudier, J., and E. Chauvenet, ii, 174.
 Chauvenet, E. See J. Chaudier.
 Chemische Fabrik auf Aktien vorm. E. Schering, i, 164.
 Chevalier, J., ii, 235.
 Ciamician, G. L., and C. Ravenna, ii, 234.
 Ciusa, R., and M. Padoa, i, 196.
 Clarke, H. T., TRANS., 416.
 Coehn, A., and H. Becker, ii, 173.
 Cohen, E., and J. F. Kröner, ii, 199.
 Cohen, E., and H. R. Kruyt, ii, 178.
 Cohen, J. B., and J. Marshall, TRANS., 328.
 Contardi, A., i, 157.
 Coppadoro, A., ii, 197.
 Creighton, H. J. M. See A. Findlay.
 Crossley, A. W., and C. Gilling, TRANS., 518.
 Cumming, A. C., TRANS., 593.
 Cushman, A. R., ii, 224.
 Cusmano, G., i, 182.

D.

Dakin, H. D., ii, 228.
 D'Ans, J., ii, 213.
 Das, T. N., ii, 209, 238.
 Deiss, E., ii, 213.
 Deutsche Gold- & Silber-Scheide-Anstalt, i, 164.
 Deventer, C. M. van, and H. J. van Lummel, ii, 179.
 Dixon, A. E., and J. Taylor, TRANS., 374.
 Dolezalek, F., ii, 134.
 Dony-Hénault, O., ii, 209.
 Dorylaud, C. J. T. See W. E. King.
 Duparc, L., R. Sabot, and M. Wunder, ii, 221.
 Dupont, J. See Roure-Bertrand Fils.
 Dutillh, H., i, 188.

Ehrenberg, P., ii, 236.
 Einhorn, A., i, 170.
 Einhorn, A., K. Fiedler, C. Ladisch, and E. Uhlfelder, i, 171.
 Einhorn, A., and E. Uhlfelder, i, 170, 172.
 Eissler, F. See S. Bondi.
 Elvert, H. See W. Wislicenus.
 Embley, E. H., ii, 228.
 Emich, F., ii, 237.
 Engler, C., i, 160.
 Engler, C., and R. Halmi, i, 160.

Engler, C., and O. Kugrala, i, 160.
 Ephraim, F., and M. Brand, ii, 207.
 Ephraim, F., and M. Gurewitsch, ii, 198.
 Ephraim, F., and H. Herschfinkel, ii, 208.
 Ephraim, F., and E. Majler, ii, 206.
 Epstein, F., and P. Krassa, ii, 202.
 Erlenmeyer, E., i, 175.

F.

Faust, O., and G. Tammann, ii, 189.
 Fenton, H. J. H., ii, 244.
 Fiebig, P., ii, 170.
 Fiedler, K. See A. Einhorn.
 Findlay, A., and H. J. M. Creighton, TRANS., 536.
 Finke, W., ii, 179.
 Flint, H. A. See C. L. Jackson.
 Foa, I., i, 187.
 Förster, P. See G. Frerichs.
 Fouquet, G., ii, 193.
 Fox, J. J., and A. J. H. Gauge, TRANS., 377.
 Francis, A. G. See Sir E. Thorpe.
 Frank, F., and K. Birkner, ii, 244.
 Frei, W., ii, 177.
 Frerichs, G., and P. Förster, i, 190.
 Friedländer, P., i, 176.
 Friedländer, P. See also A. Bezdzik.
 Fries, K., and W. Pfaffendorff, i, 186.
 Fröhlich, A., and O. Loewi, ii, 228.
 Frumina, Mlle. C., i, 150.

G.

Gabriel, S., i, 190.
 Gaillard, G., ii, 193.
 Gauge, A. J. H. See J. J. Fox.
 Gernez, D., ii, 173.
 Gesellschaft für Chemische Industrie in Basel, i, 206.
 Ghosh, A. C. See P. C. Ray.
 Gildemeister, E., and H. Kohler, i, 180.
 Gildemeister, E., and W. Müller, i, 185.
 Gilling, C. See A. W. Crossley.
 Giollitti, F., and O. Ceccarelli, ii, 217.
 Giovetti, R. See G. Ponzio.
 Gungano, L. See F. Marino-Zuco.
 Goldschmidt, V. M. See C. N. Riiber.
 Goldthwaite, N. E., ii, 224.
 Gorce, P. dela. See F. Laporte.

Goujon. See Reuillard.
Grassi, U. H. 196.
Guerbet, M., i, 149.
Gupta, N., i, 209.
Gurewitsch, M. See F. Ephraim.

H.

Haas, K. See C. Bülow.
Hahn, A., ii, 188.
Hairs, E., ii, 284.
Halmai, B. See C. Engler.
Hammers, M. See A. Naumann.
Hantzsch, A., i, 200.
Hantzsch, A., and J. Heilbron, i, 198.
Hantzsch, A., and K. Meisenburg, ii, 169.
Hantzsch, A., and P. W. Robertson, i, 203.
Hantzsch, A., and R. Robison, i, 196, 200.
Harding, V. J., and W. N. Haworth, TRANS. 488.
Hartmann, W. See C. Paal.
Hauser, O., ii, 221.
Haworth, W. N. See V. J. Harding.
Heilbron, J. See A. Hantzsch.
Heintz, W. See H. Matthes.
Hemselech, G. A., and C. de Wattleville, ii, 172.
Henderson, Y., ii, 227.
Henninger, E. See A. Naumann.
Herschfinkel, H. See F. Ephraim.
Herscovici, B. See A. Stock.
Herz, W., ii, 192.
Heubner, W., and G. Wiegner, ii, 240.
Heusler, F., ii, 179.
Hewitt, J. T., and F. B. Thole, TRANS. 511.
Hilditch, W. W. See L. B. Mendel.
Hinsberg, O., i, 164.
Hoffmann, La Roche & Co., F., i, 167.
Hoffmann, M. K., ii, 196.
Hofmann, K. A., and H. Kirmreuther, ii, 171.
Hofmann, K. A., H. Kirmreuther, and A. Thal, i, 168.
Hofmann, K. A., H. Lecher, and A. Metzler, i, 187.
Hohmann, K., ii, 237.
Holderer, M., i, 212.
Holderer, M. See also G. Bertrand.
Holliger, M., ii, 239.
Hollnagel, H. See H. Rubens.
Holmberg, B., i, 150, 165.
Horton, F., ii, 176.

Jaques, J., and W. Brassert, i, 170.
Howard, H., ii, 239.

J.

Jackson, C. L., and H. A. Flint, i, 177.
Jacobsohn, W. See C. Mannich.
Jones, H. Chapman, TRANS. 336.
Jones, H. Clary, and W. W. Strong, ii, 172.
Jones, H. O., and E. J. White, TRANS. 632.
Joseph, D. R., and S. J. Meltzer, ii, 228.
Junkersdorf, P., ii, 225.
Junkersdorf, P. See also E. Pflüger.
Jurrisen, A. W. See E. Berl.

K.

Kablukoff, I. A., and A. Sachanoff, i, 163.
Karandeff, B., i, 151.
Kaufler, F., i, 151.
Ketron, L. W. See J. M. Wolfsohn.
King, W. E., and C. J. T. Doryland, ii, 231.
Kirmreuther, H. See K. A. Hofmann.
Knott, C. G., ii, 187.
Köhler, H. See E. Gildemeister.
Kötz, A., i, 151.
Kohn-Abrest, E., ii, 212.
Kooper, W. D. See R. Otto.
Krainsky, A., ii, 286.
Krantz, L. See E. Vongerichten.
Krassa, P. See F. Epstein.
Kröner, J. F. See E. Cohen.
Kruyt, H. R., ii, 195.
Kruyt, H. R. See also R. Cohen.
Küster, W., i, 210.
Kuntzen, H. See R. Meldola.
Kusserow, R., ii, 231.

L.

Labaune, L. See Roure-Bertrand Fils.
Ladisch, C. See A. Einhorn.
Landauer, P., and H. Weil, i, 202.
Laporte, F., and P. de la Gorce, ii, 178.
Lebedeff, A. J., ii, 229.
Lecher, H. See K. A. Hofmann.
Lehmann, O., ii, 193, 194.
Leimbach, R., i, 186.
Leopold, G. H., ii, 190.

Leroide, J. See Boure-Bertrand
Fils.
Lespiau, R., i, 149.
Levi, M. G. See R. Nasini.
Liebermann, C., and H. Trucksäss,
i, 175.
Lindberg, S. See E. Bamberger.
Lippmann, E., i, 149.
Lipschütz, A., ii, 224, 227.
Loewi, O. See A. Fröhlich.
Lombard, M., ii, 197.
Lorenz, R., ii, 179.
Luckhardt, A. B., ii, 226.
Lummel, H. J. van. See C. M. van
Deventer.
Lumpp, H. See J. Schmidt.
Lusk, G. See A. I. Ringer.
Lusky, H. O., ii, 226.
Lux, E. See J. Tröger.

M.

McBain, J. W., and Miss M. Taylor,
ii, 177.
McCay, D. See W. D. Sutherland.
McCrudden, F. H., ii, 243.
McKenzie, A., and H. Wren, TRANS.,
473.
Maier, R., ii, 183.
Majler, E. See F. Ephraim.
Mameli, E., ii, 182.
Mannich, C., and W. Jacobsohn,
i, 167.
Mansfield, G., ii, 222.
Marchlewski, L., i, 188.
Marchlewski, L., and J. Robel,
i, 206.
Marckwald, W., ii, 221.
Marino-Zuco, F., and L. Giuganino,
ii, 223.
Marsden, Miss E. G. See E. C. C.
Baly.
Marshall, J. See J. B. Cohen.
Martin, A. See L. Weiss.
Mason, F. A. See F. D. Chattaway.
Matthes, H., and W. Heintz, i, 149.
Maurain, C., and G. Warcollier,
ii, 231.
Meisenburg, K. See A. Hantzsch.
Meldola, R., and H. Kuntzen,
TRANS., 444.
Meltzer, S. J. See D. R. Joseph.
Mendel, L. B., and W. W. Hilditch,
ii, 223.
Metzler, A. See K. A. Hofmann.
Meyer, G. M., i, 209.
Meyer, J., ii, 82.
Meyer, Kirstine, ii, 186.
Meyer, Kurt, i, 211.
Meyer, K. H., i, 179.

Meyerstein, W., ii, 223.
Michael, A., ii, 196.
Micheels, H., ii, 232.
Millosevic, F., ii, 221.
Mitscherlich, E. A., ii, 236.
Moore, B., F. W. Baker-Young,
Miss S. C. M. Sowton, and A.
Webster, ii, 228.
Mourou, C., and J. C. Bongrand,
i, 159.
Müller, W. See E. Gildemeister
and H. Walbaum.

N.

Nasini, R., F. Ageno, and M. G.
Levi, ii, 222.
Natanson, L., ii, 170.
Naumann, A. M. Hamers, and E.
Henninger, ii, 211.
Neuberg, C., and H. Pollak, i, 157.
Neumann, E. See L. Weiss.
Nishi, M., ii, 227.
Noelting, F. A. M., i, 176.
Nombrot, L., i, 206.

O.

Oberreit, E., i, 201.
Oechserde Coninck, W., i, 198.
Ostromisslensky, I., i, 161.
Ostwald, W., ii, 194.
Otto, R., and W. D. Kooper, ii, 233.

P.

Paal, C., and W. Hartmann, ii, 237.
Padoa, M. See R. Ciusa.
Palache, C., ii, 219.
Pascal, P., ii, 179.
Pennington, M. E., ii, 224.
Perrédes, P. E. F., ii, 196.
Petrenko-Kritschenko, P. I., i, 177.
Petrenko-Kritschenko, P. I., and
J. Schöttle, i, 188.
Pfaffendorff, W. See K. Fries.
Pflüger, E., ii, 225.
Pflüger, E., and P. Junkersdorf,
ii, 225.
Pollak, H. See O. Neuberg.
Polstorff, K., ii, 234.
Ponzio, G., i, 192.
Ponzio, G., and R. Giovetti, i, 194.
Poolc, H. H., ii, 176.
Preuss, G., ii, 238.
Price, Miss G. M. See J. F. Spencer.

Pring, J. N., TRANS.
 Pringsheim, E. See H. Pringsheim.
 Pringsheim, H., ii, 290.
 Pringsheim, H., and E. Pringsheim,
 ii, 290.
 Protz, L., ii, 187.
 Prussak, Mlle. G., ii, 229.
 Purvis, J. E., TRANS., 644.

R.

Ragg, M., i, 154.
 Rambach, F. See S. F. Schemtschuschny.
 Rankin, A. C., ii, 232.
 Rankine, A. O., ii, 193.
 Ransome, F. L. See W. T. Schaller.
 Rassenfosse, A., ii, 210.
 Ravenna, C., and M. Zamorami,
 ii, 235.
 Ravenna, C. See also G. L. Ciamician.
 Ray, P. C. TRANS., 326.
 Ray, P. C., and A. C. Ghosh, TRANS.,
 323.
 Reichard, C., i, 187.
 Reid, E. E., i, 169.
 Reiber, C. N., and V. M. Goldschmidt, i, 174.
 Ringer, A. I., and G. Lusk, ii, 227.
 Rinne, F., ii, 193.
 Ritter, R., ii, 290.
 Roaf, H. E., i, 209.
 Robel, J. See L. Marchlewski.
 Robertson, P. W. See A. Hantzsch.
 Robinson, W. O. See F. K. Cameron.
 Robison, R. See A. Hantzsch.
 Röhrig, A., ii, 235.
 Rouillard and Gonjon, ii, 239.
 Roure-Bertrand Fils, J. Dupont,
 L. Labaune, and J. Leroide,
 i, 184.
 Routala, O. See C. Engler, i, 160.
 Rubens, H., and H. Hollnagel,
 ii, 172.
 Rudolph, M. See A. Stock.
 Ruer, R., ii, 194.
 Ruhemann, S., TRANS., 457, 462.
 Rupe, H., and J. Bürgin, i, 161.
 Rupp, E., ii, 243.
 Russenberger, J. H., ii, 189.
 Rutherford, E., ii, 175.
 Rutherford, E., and B. B. Boltwood,
 ii, 175.
 Ryschenko, P., i, 181.

S.

Sabot, R. See L. Duparc.
 Sachanoff, A. See I. A. Kablu-koff.
 Sackur, O., ii, 214, 215.
 Sadikoff, W. S., i, 211.
 Saposchnikoff, A. V., i, 156; ii, 182,
 200.
 Sarthou, F., ii, 226.
 Schaller, W. T., and F. L. Ransome
 ii, 220.
 Schemtschuschny, S. F., and F.
 Rambach, ii, 204.
 Schimpff, H., ii, 181.
 Schmidt, J., and H. Lump, i, 165.
 Schöttle, J. See P. I. Petrenko-Kritschenko.
 Schreinemakers, F. A. H., ii, 195.
 Schükareff, A. N., ii, 192.
 Schulz, H., ii, 225.
 Schurakovsky, E., i, 168.
 Selvatici, E., ii, 209.
 Semmler, F. W., i, 181.
 Senderens, J. E., i, 179.
 Senter, G., TRANS., 346.
 Serkoff, S. W., ii, 177.
 Siebenrock, E. von, i, 150.
 Simpson, G. C. E., ii, 225.
 Skraup, Z. H., ii, 191.
 Smiles, S. See E. de B. Barnett.
 Smith, C., and Miss C. H. Watts,
 TRANS., 562.
 Smits, A., ii, 195.
 Soddy, F., and A. J. Berry, ii, 180.
 Sornay, P. de, ii, 243.
 Sowton, Miss S. C. M. See B. Moore.
 Späth, E. See R. Wegscheider.
 Spencer, J. F., and Miss G. M. Price,
 TRANS., 385.
 Spring, W., i, 153.
 Steiner, H. See W. Biltz.
 Stephenson, H. H., ii, 242.
 Stimmelmayer, A. See L. Weiss.
 Stock, A., and B. Herscovici,
 ii, 201.
 Stock, A., and M. Rudolph, ii, 200.
 Stoltzenberg, H., ii, 182.
 Story, W. E., ii, 184.
 Strong, W. W. See H. C. Jones.
 Strutt, R. J., ii, 175.
 Sutherland, W. D., and D. McCay,
 ii, 223.
 Svetošlavsky, W., ii, 187.
 Swain, R. E., and W. G. Bateman,
 ii, 229.
 Świętosławski, W. See Svetošlavsky.

* T.

- Tacke, B., ii, 231.
 Tammann, G. See O. Faust.
 Tanatar, S., ii, 203.
 Taylor, J. See A. E. Dixon.
 Taylor, Miss M. See J. W. McBain.
 Tereschin, E., ii, 190.
 Thal, A. See K. A. Hofmann.
 Thole, F. B. See J. T. Hewitt.
 Thorpe, Sir E., and A. G. Francis,
 ii, 209.
 Thovet, J., ii, 191.
 Touplain, F. See F. Bordas.
 Trillat, A., ii, 232.
 Träger, J., and E. Lux, i, 161.
 Troger, J., and A. Westerkamp,
 i, 207.
 Trucksäss, H. See C. Liebermann.
 Tuck, W. B. See E. C. C. Baly.
 Tyrer, D., TRANS., 621.

U.

- Uhlfelder, E. See A. Einhorn.
 Ullmann, F., and E. Cassirer,
 i, 201.
 Usher, F. L., TRANS., 389.

V.

- Vaillant, P., ii, 186.
 Vanstone, E., TRANS., 429.
 Veley, V. H., and A. D. Waller,
 ii, 228.
 Verneuil, A., ii, 212.
 Vongerichten, E., and L. Krantz,
 i, 201.

W.

- Walbaum, H., ii, 235.
 Walbaum, H., and W. Müller, i, 184.

- Wallaer, B. C., ii, 208.
 Waller, A. D. See V. H. Veley.
 Warcollier, G. See C. Maurain.
 Watteville, C. de. See G. A. Hem-
 salech.
 Watts, Miss C. H. See C. Smith.
 Webster, A. See B. Moore.
 Wedekind, E., ii, 218.
 Wegscheider, R., and E. Späth,
 i, 155.
 Weigert, F., ii, 174.
 Weil, H., ii, 242.
 Weil, H. See also P. Landauer.
 Weiss, L., A. Martin, and A. Stim-
 melmayr, ii, 216.
 Weiss, L., and E. Neumann, ii, 217.
 Weisweiler, G. See G. Bertrand.
 Westerkamp, A. See J. Trögen.
 White, E. J. See H. O. Jones.
 Whittelsey, T., i, 184.
 Wiegner, G. See W. Heubner.
 Wilke-Dörfurt, E., ii, 204.
 Wilkie, J. M., ii, 240.
 Wilson, W., ii, 175.
 Wislicenus, W., and H. Elvert,
 i, 158.
 Wolffsohn, J. M., and L. W. Ketron,
 ii, 222.
 Woodyatt, R. T., ii, 227.
 Wootton, W. O., TRANS., 405.
 Wren, H. See A. McKenzie.
 Wunder, M. See L. Duparc.

Y.

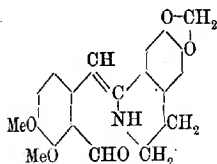
- Yvon, P., i, 163.

Z.

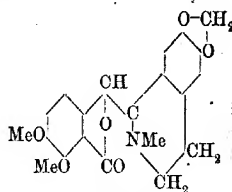
- Zamorani, M. See C. Ravenna.
 Zani, V., ii, 219.
 Zickendraht, H., ii, 171.
 Ziegler, J. See H. Bechhold.

1904, 37, 3335 and 4573) and, when treated with a large excess of alkali, is reduced to dihydroberberine and simultaneously oxidised to hydroxyberberine, the aldehyde grouping being converted into $\cdot\text{CH}_2(\text{OH})$ and $\cdot\text{CO}_2\text{H}$ in the manner characteristic of aromatic aldehydes.

The proposed modification of the positions of the methoxy-groups in the berberine formula receives further confirmation from the consideration that berberine occurs along with hydrastine in *hydrastis canadensis*, and the close relationship between these alkaloids becomes very striking if the new formula for berberinal is placed by the side of that of hydrastine:



Berberinal.



Hydrastine.

These alkaloids are, indeed, so closely related as to suggest that hydrastine is either formed in the plant from berberine, or that they are both derived from some common parent.

THE UNIVERSITY,
MANCHESTER.

XXXIV.—*Decomposition of Dimercurammonium Nitrite by Heat.*

By PRAFULLA CHANDRA RAY and ATUL CHANDRA GHOSH.

THE preparation of dimercurammonium nitrite has been already described at some length (Trans., 1902, 81, 644), and evidence has been adduced in support of the view that it is a derivative of ammonium nitrite.

The solution of sodium mercuric nitrite, from which it is obtained by the action of ammonia, does not contain mercury as cation, but as part of a complex anion; it does not, therefore, undergo the hydrolysis so characteristic of oxylic mercuric salts, and has presumably a non-oxylic constitution. Two samples of the salt were prepared, and dried at 95° for analysis:

Found: Hg = (I) 84.74; (II) 84.95. N = (I) 6.33; (II) 6.16.

$\text{NHg}_2\text{NO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ requires Hg = 85.29. N = 5.97 per cent.

Method of Experiment.—From 0.2 to 0.6 gram of salt was placed in a small bulb, the drawn-out stem of which was connected with a Sprengel pump. A preliminary trial proved that the salt commenced to decompose, although very slowly, at about 140° , and that even at 210° a portion of it remained undecomposed. The bulb was therefore cautiously and gradually immersed in a bath of molten sodium and potassium nitrates, mixed in about equal proportions (m. p. 218°). The temperature was slowly raised to 250° , when no more gas was evolved, the "click" in the fall-tube remaining persistent. Raising the temperature to 280° made no difference in this respect. The gas which was evolved was found to consist of a mixture of nitrous oxide, nitrogen, and oxygen; nitrous fumes were not noticed; in fact, the mercury in the fall-tube was not in the least tarnished, nor could even a trace of nitric oxide be detected. If, however, the bulb was suddenly plunged in a bath previously heated to 225° , the mode of decomposition was slightly different. Mercury in the shape of fine dust was at once deposited on the glass, and in the gaseous mixture nitric oxide could be recognised.

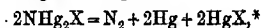
The nitrous oxide was removed by alcohol, and sometimes by repeated shaking with cold water, until no more absorption took place. The oxygen was in some instances removed by alkaline pyrogallate, but generally by means of phosphorus. The residue in the bulb was of a greyish-yellow colour; it consisted mainly of mercuric oxide with a small proportion of mercuric nitrate. This was proved by boiling the mixture with a solution of sodium hydroxide. The filtrate indicated the presence of nitrogen in the form of nitrate. Metallic mercury, both as a mirror and in fine globules, was deposited in the stem of the bulb. More than a dozen experiments were performed, the results of some of which are tabulated below:

"Free" N.	N as N_2O .	N as $\text{Hg}(\text{NO}_3)_2$.	Oxygen.	Total O in the salt.	Hg as $\text{Hg}(\text{NO}_3)_2$.	Hg as HgO .	"Free" Hg.
I. 3.21	1.55	1.21	0.21	8.82	8.64	57.20	19.45
II. 3.17	1.48	1.32	0.17	—	9.43	55.31	20.55
III. 3.43	1.44	1.10	0.22	—	6.00	62.65	16.68
IV. 3.53	1.60	0.84	0.34	—	5.14	63.31	16.84
V. 3.73	1.52	0.72	0.25	—			

In those experiments in which nitric oxide was obtained, the nitrogen was distributed as follows:

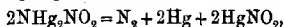
	"Free" N.	N as N_2O .	N as $\text{Hg}(\text{NO}_3)_2$.	N as NO .
I.	2.54	1.03	2.31	0.09
II.	3.22	2.24	0.29	0.22
III.	2.69	1.95	0.95	0.38

Discussion of Results.—It has already been pointed out that the halogen derivatives of the mercurammonium group (NHg_2^-) may be regarded as non-oxylc in constitution, since they decompose under the action of heat according to the equation :



where $\text{X} = \text{Cl}$ or Br .

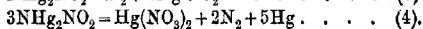
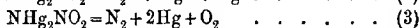
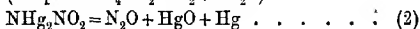
From analogy, one would naturally expect that the nitrite of the series should decompose as follows :



and that the mercurous nitrite thus formed, being unstable at this temperature, would yield its own products of decomposition (compare Ray and Sen, Trans., 1903, 83, 491). We have repeated the experiment on the decomposition of mercurous nitrite. The initial temperature of decomposition has been found to be almost the same as that of dimercurammonium nitrite, namely, 140° , and it is completed at 247° . In order to protect the mercury in the Sprengel pump from being soiled, a glass spiral, packed with glass beads and moistened with sodium hydroxide solution, was interposed, as in some of the previous experiments (compare Trans., 1905, 87, 180). The gaseous product which was collected was found to be nitric oxide. Moreover, had dimercurammonium nitrite decomposed according to the equation given above, exactly half the nitrogen would have been given off as "free" nitrogen, but it varies from 3.2 to 3.7 per cent. The formation of nitrous oxide is rather remarkable. The reaction evidently seems to proceed in three or four directions simultaneously, which may be expressed by the following equations :



(compare $\text{NH}_4\text{NO}_2 = \text{N}_2 + 2\text{H}_2\text{O}$)



We are at present engaged in studying the decomposition of dimercurammonium nitrate, in the hope that further light may be thrown on these points.

CHEMICAL LABORATORY,
PRESIDENCY COLLEGE, CALCUTTA.

Ray, "Studien über die Konstitution der Dimerkurammonium Salze" (*Zeitsch. anorg. Chem.*, 1902, 33, 193; also, Sen, *ibid.*, 197).

XXXV.—The Double Nitrites of Mercury and the Metals of the Alkaline Earths.

By PRAFULLA CHANDRA RAY.

In a previous communication a general method of preparation of the double nitrites of mercury and the alkali metals has been described (Trans., 1907, 91, 2031). Recently it has been found that this method is equally applicable to the preparation of the corresponding mercuric calcium, mercuric strontium, and mercuric barium nitrites. For instance, if a solution of calcium nitrite is added to a perfectly clear solution of mercurous-mercuric nitrite, $(\text{HgNO}_2)_2 \cdot 4\text{Hg}(\text{NO}_2)_2$, almost immediate turbidity is caused, due to the separation of metallic mercury in a fine state of division. The explanation already given (*loc. cit.*), namely, that "the process of dissociation is accelerated because of the tendency of one of the products of dissociation, namely, mercuric nitrite, to unite with the alkali nitrite," admits of further amplification. It is the tendency to form complex ions that is really the *motif* of the reaction. A solution of potassium mercuric nitrite, $\text{K}_2\text{Hg}(\text{NO}_2)_6$, contains mercury, not as a cation, but as part of a complex bivalent anion, $\text{Hg}(\text{NO}_2)_4^{2-}$. Hence, such a solution behaves as a neutral one, and can be diluted *ad infinitum* without undergoing the hydrolysis, so characteristic of the oxy-salts of mercury, for example, mercuric nitrate. This also explains the singular behaviour which I noticed some twelve years ago (*Zeitsch. anorg. Chem.*, 1896, 12, 367), namely, that carbamide does not precipitate the mercury from the solution, or a solution of sodium sulphate give the characteristic precipitate of turpeth mineral.

Method of Preparation.—The light yellow solution of the double nitrites is evaporated under diminished pressure over sulphuric acid. As a rule, crystallisation of the salts does not take place, but a syrupy liquid is obtained, which, on being stirred with a rod, solidifies entirely, with the formation of mealy crystals and liberation of heat. In fact, the characteristic behaviour of supersaturated solutions is noticed. As the crystals were very soluble, they were washed with the minimum quantity of water, and dried by pressure between folds of bibulous paper. If the salts are preserved in a stoppered bottle without being well dried, they slowly decompose, with evolution of nitrous fumes; but if they are kept in the open bottle in the desiccator, they remain perfectly stable (compare mercuric

* Hans Pick, "Beiträge zur Charakteristik des Nitrit-ions. Der Quecksilber nitrit-komplex" (*Diss.*, Breslau, 1906).

nitrite. These compounds, like the compounds described below, contain five molecules of water of crystallisation.

Mercuric Calcium Nitrite.

Found: Hg = 38.21; Ca = 7.96; N = 10.98.

$\text{Hg}(\text{NO}_2)_2 \cdot \text{Ca}(\text{NO}_2)_2 \cdot 5\text{H}_2\text{O}$ requires Hg = 38.91; Ca = 7.78;
N = 10.90 per cent.

Mercuric Strontium Nitrite.

Found: Hg = 44.58; Sr = 13.08; N = 11.17.

$3 \text{Hg}(\text{NO}_2)_2 \cdot 2\text{Sr}(\text{NO}_2)_2 \cdot 5\text{H}_2\text{O}$ requires Hg = 45.31; Sr = 13.18;
N = 10.57 per cent.

Mercuric Barium Nitrite.

Found: Hg = 39.88; Ba = 19.80; N = 10.55.

$3\text{Hg}(\text{NO}_2)_2 \cdot 2\text{Ba}(\text{NO}_2)_2 \cdot 5\text{H}_2\text{O}$ requires Hg = 42.13; Ba = 19.24;
N = 9.84 per cent.

The preparation of the last two salts was repeated, but the composition was practically constant. The low percentage of mercury and the proportionately high percentages of barium and of nitrogen in the last one are probably due to the substance being invariably contaminated with traces of mother liquor containing excess of the nitrites of the latter metal.

On comparing the whole series of double nitrites, it is of interest to note that the power of mercuric nitrite to unite with the nitrites of the alkali metals is the greater the less the atomic weights of the latter. Thus, mercuric nitrite can combine with four molecules of lithium nitrite and with three molecules of potassium nitrite, although it also forms characteristic stable compounds with two molecules of either sodium or potassium nitrite. On the other hand, it combines molecule for molecule with calcium nitrite. Again, one molecule of mercuric nitrite can combine with only two-thirds of a molecule of strontium or barium nitrite. Cryoscopic determinations of the molecular weights of the above salts have been undertaken with the view of throwing light on their constitution, the results of which I hope to communicate shortly.

CHEMICAL LABORATORY,
PRESIDENCY COLLEGE, CALCUTTA.

XXXVI.—The Constitution of the Amidines. A New Method for Determining Molecular Symmetry.

By JULIUS BEREND COHEN and JOSEPH MARSHALL.

H. VON PECHMANN (*Ber.*, 1895, 28, 869) made the observation that the amidine (I) prepared from benzanilide iminochloride and *p*-toluidine was identical, so far as could be shown by comparison of melting points and other physical properties with the amidine (II) obtained from benzoyl-*p*-toluidide iminochloride and aniline,



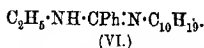
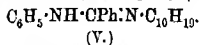
The product obtained by the ethylation of this substance was shown to be a mixture of two ethyl derivatives in equal quantities, and these were separable by mechanical means. This fact may indicate, either that the original amidine is a mixture of equal quantities of the substances represented by (I) and (II), or that it has a varying structure caused by the oscillation of the hydrogen atom marked * in the formula between the two nitrogen atoms.

In cases where the two bases differed in character from each other, von Pechmann obtained quite different results. Using (a) methylbenzamide iminochloride and aniline, and (b) benzanilide iminochloride and methylamine, he obtained, as before, the same product in each case, but methylation of this substance produced only one methyl derivative. This was found to be identical with the amidine obtained by combining methylbenzamide iminochloride with methylaniline, indicating that the amidine prepared either by method (a) or (b) had the constitution represented by (III), and that a substance with the formula (IV) was not produced at all.



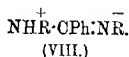
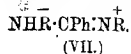
The present investigation was undertaken with the view of determining whether the introduction of optically active groups into the amidine would afford a more delicate means of distinguishing between the products of the two reactions in the event of their being indistinguishable by other means. The optically active base used in most of the experiments was *l*-menthylamine, as being easily obtainable in large quantities (Tutin and Kipping, *Trans.*, 1904, 85, 69). The benzoyl derivative of menthylamine was converted into the iminochloride and allowed to react with the second base, and the amidine obtained in this way was compared with that prepared from the iminochloride of the benzoyl derivative of the second base and menthylamine. The

other bases used were aniline, *o*-, *m*-, and *p*-toluidine, and ethylamine. It was found that in all cases the pairs of amidines had exactly the same specific rotations, melting points, and other physical properties. It was also shown, by ethylation of some of the amidines, that they were single substances and not mixtures, as only one ethyl derivative was formed in each case. These ethyl derivatives were also synthesised, and it was proved that the constitution of the amidine containing phenyl and menthyl groups is represented by (V), and that containing ethyl and menthyl groups by (VI).

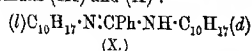
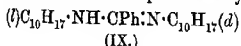


These experiments confirm the observation that marked difference in character of the radicles causes the formation of one and the same product in the two reactions, and there is no indication of any equilibrium mixture, as in the case where the radicles are of the same type. It is interesting to note that the hydrogen atom is in all cases attached to the nitrogen atom in the less basic group.

It was then thought that it would be of interest to prepare an amidine in which the two bases were enantiomorphous. In such a case, according to von Pechmann, a mixture of two substances would be obtained of the types (VII) and (VIII).



These should be produced in equal quantities, and hence any optical activity due to (VII) would be counterbalanced by that due to (VIII), and the product should be inactive. This was found to be the case, the bases used being *d*- and *l*-bornylamines, which are easily obtained by Forster's method (Trans., 1898, 73, 390) from the corresponding camphors. Ethylation of the amidine produced one inactive ethyl derivative. It was conceivable that if the amidine were a mixture of two substances represented by formulæ (IX) and (X) :



it might be possible by crystallising it with an optically active acid to obtain fractions which would, after removal of the acid, be active. The amidine was combined with Reychler's *d*-camphorsulphonic acid, and the salt crystallised several times from hot light petroleum. The specific rotations of various fractions were then determined, but they were found to be practically identical. After removal of the acid, the recovered amidine was inactive. Similar experiments were carried out with the ethyl derivative, but no resolution of the amidine could be detected.

It is proposed to extend to other classes of compounds this method

of examining molecular symmetry by the means of enantiomorphous radicles into different positions in the molecule. It is at present engaged in determining the space formula of quinquavalent nitrogen by the aid of this method.

EXPERIMENTAL.

Phenylmenthylbenzamidine, $C_{10}H_{19} \cdot N:C(C_6H_5) \cdot NH \cdot C_6H_5$, was prepared by boiling in light petroleum the iminochloride obtained from 5 grams of benzanilide with 7.5 grams of *L*-menthylamine. The menthylamine hydrochloride which separated was collected, the light petroleum removed, and the gummy residue extracted with dilute hydrochloric acid. To the filtered acid solution, sodium hydroxide was added, and the amidine extracted with ether. It was crystallised from alcohol, and formed fine needles melting at $110-111^\circ$:

0.5072 in 20 c.c. chloroform gave, in a 2-dm. tube, $\alpha_D - 7.49^\circ$; whence $[\alpha]_D^{25} - 146^\circ$.

The same compound was obtained by boiling the light petroleum solution of the iminochloride from 5 grams of benzoylmenthylamide with 3.6 grams of aniline. The hydrochloride of the amidine which separated was collected, washed with a little more ether, and decomposed with sodium hydroxide. The compound obtained after recrystallisation from alcohol melted at $110-111^\circ$, and a mixture of this substance with that obtained in the previous experiment had the same melting point:

0.5104 in 20 c.c. chloroform gave, in a 2-dm. tube, $\alpha_D - 7.44^\circ$; whence $[\alpha]_D^{25} - 146^\circ$.

0.2054 gave 15 c.c. N_2 at 15° and 750 mm. $N = 8.61$.

$C_{22}H_{30}N_2$ requires $N = 8.39$ per cent.

The *hydrochloride*, prepared from both specimens, melted at 224° , and formed long needles when crystallised from dilute alcohol. It was only slightly soluble in cold, but fairly so in hot, water.

The *platinichloride* was precipitated in a crystalline condition by adding platinum chloride to a dilute alcoholic solution of the hydrochloride. It melts at 213° :

0.5504 gave 0.0998 Pt. M.W. of amidine = 333.

$C_{22}H_{30}N_2$ requires M.W. = 334.

Ethylation of Phenylmenthylbenzamidine.

2.3 Grams of the pure amidine were heated on the water-bath for ten hours with an excess of ethyl iodide, the latter being then distilled. The residue, consisting of the hydriodide of the ethylated amidine, crystallised, and was decomposed with sodium hydroxide. After two

crystallisations from alcohol. 1.5 grams of pure substance were obtained in beautiful square plates, which melted at 66–67°. The substance was perfectly homogeneous:

0.3596 in 25 c.c. chloroform gave, in a 2-dcm. tube, $\alpha_D - 11.28^\circ$;
whence $[\alpha]_D^{20} - 392^\circ$.

0.6260 in 25 c.c. chloroform gave, in a 0.502-dcm. tube, $\alpha_D - 11.28^\circ$;
whence $[\alpha]_D^{20} - 391^\circ$.

This amidine was also produced by treating benzoylmenthylamide iminochloride with ethylaniline. The characteristic plates, melting at 66–67°, were obtained:

0.4611 in 25 c.c. chloroform gave, in a 2-dcm. tube, $[\alpha]_D - 14.47^\circ$;
whence $[\alpha]_D^{20} - 392^\circ$.

0.2164 gave 14.55 c.c. N_2 at 15° and 749 mm. $N = 7.92$.

$C_{25}H_{34}N_2$ requires $N = 7.73$ per cent.

The hydrochloride was not obtained in the crystalline condition, but only as a sticky mass, soluble in water. The hydriodide crystallises in prisms, melting at 220°. The platinichloride was precipitated from an aqueous solution of the hydrochloride, and melted at 151°:

0.5756 gave 0.0980 Pt. M.W. of amidine = 368.

$C_{25}H_{34}N_2$ requires M.W. = 362.

Phenylmenthylethylbenzamidine.

For purposes of comparison, the amidine from benzanilide iminochloride and ethylmenthylamine was prepared. It crystallised from alcohol, in which it was much less soluble than the preceding substance, in needles melting at 157°:

0.7436 in 25 c.c. chloroform gave, in a 2-dcm. tube, $\alpha_D - 3.6^\circ$;
whence $[\alpha]_D^{20} - 60.5^\circ$.

0.1645 gave 11 c.c. N_2 at 20° and 762 mm. $N = 7.73$.

$C_{25}H_{34}N_2$ requires $N = 7.73$ per cent.

The hydrochloride was insoluble in cold water, and crystallised from alcohol in needles melting at 280°.

o-Tolylmenthylbenzamidine, $C_{10}H_{19} \cdot N : C(C_6H_5) \cdot NH \cdot C_7H_7$.

This substance, prepared from benzoyl-*o*-toluidide iminochloride and menthylamine, was isolated as the hydrochloride by saturating with dry hydrogen chloride the light petroleum solution from which the precipitated menthylamine hydrochloride formed in the reaction had been separated. The precipitated gummy mass was crystallised from alcohol and decomposed with dilute aqueous sodium hydroxide. The amidine crystallises from alcohol in needles melting at 106–107°:

0.3391 in 25 c.c. chloroform gave, in a 2-dcm. tube, $\alpha_D - 2.85^\circ$;
whence $[\alpha]_D^{25} - 105^\circ$.

This amidine was also prepared from benzoylmenthylamide iminochloride and *o*-toluidine, the hydrochloride of the amidine separating from the light petroleum almost quantitatively:

0.6264 in 25 c.c. chloroform gave, in a 2-dcm. tube, $\alpha_D - 5.26^\circ$;
whence $[\alpha]_D^{25} - 105^\circ$.

0.2044 gave 13.9 c.c. N_2 at 11° and 750 mm. $N = 8.13$.

$C_{24}H_{32}N_2$ requires $N = 8.05$ per cent.

The hydrochloride crystallises from alcohol in small, rectangular plates, melting at 218° , and is scarcely soluble in water.

The platinichloride was obtained as a crystalline powder:

0.5654 gave 0.1005 Pt. M.W. of amidine = 344.

$C_{24}H_{32}N_2$ requires M.W. = 348.

m-Tolylmenthylbenzamidine was isolated in a similar manner to the *o*-tolyl derivative from benzoylmenthylamide iminochloride and *m*-toluidine. The base crystallises from alcohol in needles, and melts at $89-90^\circ$:

0.6268 in 25 c.c. chloroform gave, in a 2-dcm. tube, $\alpha_D - 7.13^\circ$;
whence $[\alpha]_D^{25} - 142^\circ$.

The amidine from benzoyl-*m*-toluidide and menthylamine had the same melting point:

0.6118 in 25 c.c. chloroform gave, in a 2-dcm. tube, $\alpha_D - 6.98^\circ$;
whence $[\alpha]_D^{25} - 143^\circ$.

0.2090 gave 14.4 c.c. N_2 at 13.5° and 751 mm. $N = 8.18$.

$C_{24}H_{32}N_2$ requires $N = 8.05$ per cent.

The hydrochloride crystallises from alcohol, and is only very slightly soluble in hot water. It melts at 232° .

The platinichloride forms very small needles, which melt at 217° :

0.5603 gave 0.0991 Pt. M.W. of amidine = 346.

$C_{24}H_{32}N_2$ requires M.W. = 348.

p-Tolylmenthylbenzamidine, isolated in the usual way from benzoylmenthylamide iminochloride and *p*-toluidine, crystallised from alcohol in stout prisms, which melted at $63-68^\circ$ even after several recrystallisations:

0.6252 in 25 c.c. chloroform gave, in a 2-dcm. tube, $\alpha_D - 6.55^\circ$;
whence $[\alpha]_D^{25} - 131^\circ$.

Repeated crystallisation had no effect on this value. When prepared from benzoyl-*p*-toluidide and menthylamine, the same rather indefinite melting point was observed:

0.6231 in 25 c.c. chloroform gave, in a 2-dcm. tube, $\alpha_D - 6.54^\circ$;
whence $[\alpha]_D^{25} - 131^\circ$.

0.2069 gave 13.9 c.c. N_2 at 15° and 747 mm. $N = 7.94$.

$C_{24}H_{33}N_2$ requires $N = 8.05$ per cent.

The *hydrochloride* crystallised from alcohol in small needles melting at 225°, and the *platinichloride*, obtained as a crystalline precipitate, melted at 208°:

0.2700 gave 0.0474 Pt. M.W. of amidine = 350.

$C_{24}H_{33}N_2$ requires M.W. = 348.

Menthylethylbenzamidine, $C_{10}H_{19} \cdot N : C(C_6H_5) \cdot NH \cdot C_2H_5$.

This substance was prepared by treating a light petroleum solution of ethylamine (2 mols.) with the calculated quantity of benzoylmenthylamide iminochloride. The ethylamine hydrochloride was collected, and, after removal of the light petroleum, the gummy residue was boiled with dilute sulphuric acid. The clear solution of the sulphate was treated with a concentrated aqueous solution of potassium iodide, and the precipitated iodide was separated and decomposed with sodium hydroxide. The amidine solidified after removal of the ether used in its extraction, but all attempts at recrystallisation were unsuccessful. The substance melted at 65—67°. It was purified by conversion into the iodide, which was again decomposed. No alteration in the melting point could be observed:

0.6282 in 25 c.c. chloroform gave, in a 2-dcm. tube, $\alpha_D - 5.63^\circ$;
whence $[\alpha]_D^{25} - 112^\circ$.

The amidine was also prepared from ethyl benzamide iminochloride and menthylamine, and this specimen had the same melting point:

0.6240 in 25 c.c. chloroform gave, in a 2-dcm. tube, $\alpha_D - 5.57^\circ$;
whence $[\alpha]_D^{25} - 112^\circ$.

0.2133 gave 16.9 c.c. N_2 at 13° and 750 mm. $N = 9.49$.

$C_{19}H_{30}N_2$ requires $N = 9.80$ per cent.

The *hydrochloride* was only obtained as a sticky mass, which was very soluble in water. The *hydriodide*, which was much less soluble, was not obtained in a crystalline condition.

The *platinichloride* formed microscopic plates, melting at 218°:

0.4816 gave 0.0968 Pt. M.W. of amidine = 280.

$C_{19}H_{30}N_2$ requires M.W. = 286.

Four grams of this amidine were boiled for ten hours with ethyl iodide, and, after distilling off the excess of alkyl iodide, the *hydriodide* of *menthylethylbenzamidine* which remained was recrystallised from water and then converted into the amidine. On crystallisation from alcohol, this formed small, rectangular plates, melting at 31—32°:

0.4756 in 25 c.c. chloroform gave, in a 2-dcm. tube, $\alpha_D - 6.53^\circ$;
whence $[\alpha]_D^{25} - 172^\circ$.

This substance was quite homogeneous and proved to be identical with the amidine prepared from benzoylmenthylamine and diethylamine.

0.470g. in 25 c.c. chloroform gave, in a 2-dcm. tube, $\alpha_D - 6.47^\circ$; whence $[\alpha]_D^{18} - 172^\circ$.

The hydrochloride was not crystalline, but the hydriodide crystallized from water in fine needles, which melted at 155° . The platinichloride melts at 180° .

Before the enantiomorphous bornylamines were selected for use in the final experiments, several attempts were made to prepare other enantiomorphous bases.

d-Dihydrocarvylamine was prepared from *d*-carvone by reduction of the oxime with sodium in alcoholic solution (Wallach, *Ber.*, 1891, 24, 3984), and the lævo-base was obtained from *d*-limonene by way of the nitrosochloride and *l*-carvoneoxime. The benzoyl derivatives were prepared, but it was found that during the reaction of phosphorus pentachloride with these substances, hydrochloric acid is added on to the molecule, and hence the use of an unsaturated base was out of the question.

As the enantiomorphous carvones are easily obtained, it was thought that the carvomenthylamines prepared by the same methods from each of these carvones would answer our purpose. Accordingly, some time was spent in attempts to obtain these bases in quantity. Baeyer's method (*Ber.*, 1893, 26, 822) was first tried, but as very unsatisfactory yields were always obtained, the method was abandoned.

Attempts were made to reduce dihydrocarvylamine to tetrahydrocarvylamine by Sabatier and Senderens' method, but, although reduction took place to some extent, the reduced product was inactive. Next, 2-amino-1-methylcyclohexane was prepared from 1-methylcyclohexan-2-one, obtained from *o*-cresol (Sabatier and Mailhe, *Compt. rend.*, 1905, 140, 350), and an attempt was made to resolve this base by fractional crystallisation of the *d*-camphorsulphonate. No satisfactory results were obtained.

Finally, the two bornylamines were prepared. The active benzoyl derivative melts at 139° , and the inactive substance at 144° .

d-Bornyl-*l*-bornylbenzamidine.

The iminochloride of benzoyl-*l*-bornylamide was prepared in the usual way, and treated with a light petroleum solution of *d*-bornylamine. The amidine was isolated and crystallised from alcohol, from which it separated in small prisms (often in stellate clusters), melting at $93-94^\circ$.

The substance was identical with the original amine in every respect with the exception of benzoyl-d-bornylamide, iminochloride, and d-bornylamine.

0.2013 gave 12.4 c.c. N_2 at 12.5° and 731 mm. $N = 7.15$.

$C_{27}H_{40}N_2$ requires $N = 7.14$ per cent.

The *hydrochloride* crystallises from ether in long needles, which melt at 297°. It is very soluble in alcohol. The *platinichloride* melts at 215°. The *sulphate* was obtained as fine needles from dilute alcohol, and melted at 138°. The *hydriodide* is insoluble in water, crystallises easily from absolute alcohol, and melts at 262°.

The *d-camphorsulphonate* was prepared by mixing molecular proportions of the amidine and acid dissolved in ether and alcohol respectively. The salt was crystallised several times from light petroleum, and melted at 205–206°:

1.0353 in 25 c.c. alcohol gave, in a 2-dcm. tube, $\alpha_D + 1.34^\circ$; whence $[\alpha]_D^{20} + 16.2^\circ$.

The salt was further recrystallised, but the melting point was not affected, and a determination of the specific rotation gave 16.4° . A second crop of crystals had a slightly lower melting point, and a specific rotation of 15.4° .

A quantity of the salt was mixed with ice-water, cold ether and cold sodium hydroxide solution added, and the ethereal solution of the amidine was immediately polarimetrically examined. No rotation could be observed.

Ethylation of d-Bornyl-1-bornylbenzamidine.

The amidine was heated in a sealed tube with light petroleum and excess of ethyl iodide for eight hours in a boiling-water bath. On cooling, the *hydriodide* of the ethylamidine crystallises in fine needles, melting at 257–258°, and these were recrystallised from a mixture of benzene and light petroleum and decomposed by sodium hydroxide. The amidine melted at 93–94°, and a mixture of this with the original amidine had a melting point of 91–93°. It was inactive:

0.1997 gave 12.4 c.c. N_2 at 14° and 711 mm. $N = 6.96$.

$C_{20}H_{24}N_2$ requires $N = 6.67$ per cent.

The *hydrochloride* crystallises from alcohol in needles, melting at 238°.

The *d-camphorsulphonate* was prepared as before and recrystallised; melts at 204–206°:

0.9987 in 25 c.c. alcohol gave, in a 2-dcm. tube, $\alpha_D + 1.27^\circ$; whence $[\alpha]_D^{20} + 16.1^\circ$.

The amidine recovered from this fraction of the salt was inactive,

as was also that obtained from the other fractions which were separately examined.

The authors have to thank Mr. W. H. Perkins for help in the reparation of the first amidine described in this paper.

THE UNIVERSITY,
LEEDS.

XXXVII.—*Silver Amalgams.*

By HENRY CHAPMAN JONES.

SILVER amalgams are of interest, not only because they are members of the general class of amalgams, but also because some occur in Nature, and because of the specific gravity of some of them being much higher than that of mercury. The remarkable contraction that takes place when the two metals combine was stated by Joule (*Journ. Chem. Soc.*, 1863, 16, 383) to be "referable no doubt to the assumption of the solid state by the mercury, the specific gravity of which comes out at 16.5 from these (Joule's) experiments." This high value for the specific gravity of solid mercury does not appear to have been confirmed.

The silver amalgams that have so far been examined have been of very irregular compositions when viewed as compounds, and as they have been prepared by bringing the two metals together either directly, or by allowing an excess of mercury to precipitate silver on itself from a salt solution, it is hardly possible that the amalgams obtained were homogeneous.

The object of this paper is to indicate a method by which a series of silver amalgams may be obtained of definite molecular composition (within the errors of experiment) and in a really homogeneous condition; and, further, to give some of the properties of two of them.

The method consists, in short, in the preparation of a double salt, or a molecular mixture of salts, of the two metals with subsequent reduction in the cold to the metallic condition. When mercuric chloride acts on either silver or mercury, or an amalgam of the two metals, each atom of either metal combines with a molecule of mercuric chloride. If, then, the chlorine is removed, and this is easily done by means of ferrous oxalate, the metals alone remain. In this way amalgams may be obtained in which the metals exist in the proportions indicated by the formulæ AgHg , AgHg_3 , AgHg_7 , AgHg_{15} , AgHg_{31} , AgHg_{63} , and the author has actually prepared these six amalgams, although not all of them in

quantities suitable for examination. If the product of the action of mercuric chloride on metallic silver, that is, the double chloride, AgHgCl_2 , is treated with an excess of sodium sulphite solution, half the silver and three-fourths of the mercury will be dissolved, and there will remain an amalgam of the composition represented by the formula Ag_2Hg . This, by treatment alternately with mercuric chloride and ferrous oxalate, gives another series of amalgams intermediate between the members of the series given above, namely, Ag_2Hg , AgHg_2 , AgHg_3 , AgHg_{11} , etc.

Preparation of the Amalgams.

Some details concerning this have already been published (*J. Soc. Chem. Ind.*, 1893, 12, 983). A granular sample of metallic silver reacts most readily with mercuric chloride—such preparations as are obtained by the reduction of silver salts by means of zinc in acid solutions, or by dextrose in the presence of alkali hydroxide. But metallic silver so obtained I have never found to be pure. If dried at 100° , it invariably loses something on ignition, 0.12, 0.74 per cent., and so on in different cases, although the product was well washed with dilute nitric acid and ammonia. Silver obtained by reduction with ammonium sulphite, if properly washed and dried at 100° , loses nothing on ignition, but such silver is flaky and crystalline rather than granular, and reacts less readily than the other. It is preferable, in using ammonium sulphite, to heat the mixture quickly in small portions, and so obtain the metal more finely divided than by the usual slow process.

Metallic silver and mercuric chloride will interact in many different liquids, or in no liquid, by simply shaking them together and allowing them to remain. I have always used water, but, judging from the analogous reaction with mercuric bromide, it might be possible to find a medium that would expedite the change. Mercuric bromide reacts very slowly in water, the salt being very sparingly soluble; but in benzene, in which the salt is soluble to practically the same extent, the velocity of the reaction is very remarkably increased, whilst in acetone, which very freely dissolves the mercuric bromide, the change does not appear to be so rapid as in benzene. Light petroleum dissolves much less of the mercuric salt than water does, yet under otherwise the same conditions the change will appear complete in light petroleum in a time that in water has sufficed for little more than a superficial reaction.

The reduction of the chloride by means of ferrous oxalate takes place practically at once. The reagent is obtained by pouring one volume of a saturated solution of ferrous sulphate into six volumes of a saturated solution of potassium oxalate. The large excess of

the potassium oxalate solution. The action of mercuric chloride on amalgam is accelerated, for the purpose of adding more mercury to it, is far more rapid than the action on metallic silver, presumably because the amalgam is more finely divided. If a double (or mixed) chloride of silver and mercury, contains metallic silver (an unattacked residue, for example), it will not give a constant weight at 100° , as metallic mercury is liberated by the silver and continuously volatilised.

The Amalgam AgHg.—In bulk, as dried over sulphuric acid without the aid of heat (in a steam-oven such an amalgam lost mercury at a rate equivalent to 0.47 per cent. per hour), this amalgam appears as a grey, non-adherent powder, which can be easily burnished into a metallic film. It consists of rounded particles, generally about 0.003 mm. in diameter. Some are oval and up to 0.005 mm. long, and others are as small as 0.002 mm. As diffused in cedarwood oil for microscopic examination, the particles have a marked tendency to adhere in rows, often branched, Y-shape, but the individual particles are quite distinct, and there is no appearance of a want of homogeneity. The silver mercurous chloride from which it was obtained was in similar rounded particles, but more varied in size, and on the whole rather smaller. These differences are probably accidental, and it seems almost certain that on the reduction of the chloride to the amalgam the separate particles retain their individuality. The specific gravity of the amalgam, taken in water at 20° and compared with water at 20° , was 12.8055. When pumping out the air, there appeared to be a continual evolution of gas, as if the amalgam decomposed the water. A second estimation with more stringent methods to remove air gave 12.8099. A determination in xylene showed that these figures are not low, and therefore that if the amalgam does act on the water the result is not sufficient to vitiate the determination. The calculated specific gravity, assuming no contraction when the two metals combine, is 12.29. Evidently, therefore, in the amalgam obtained as described, there is contraction on combination, but not nearly so much as in the crystalline amalgam which Joule obtained by placing mercury in silver nitrate solution. Such a preparation, which had approximately the same composition, had a specific gravity of 14.68, and another sample, obtained by adding more mercury and squeezing out as much as possible by a high pressure, gave 13.44. Other observers have found specific gravities for silver amalgams up to about 14.

The Amalgam AgHg₂.—When the amalgam AgHg is acted on by mercuric chloride, the resulting chloride (empirically AgHg₂Cl)

is not dissimilar to the double chloride, AgHgCl_2 , which persists in the amalgam AgHg , produced from it by reduction, has now gone—the particles are disintegrated. They are smaller, 0.001 mm. in diameter or less, and irregular in shape. This chloride is easily reduced, and the dried amalgam, AgHg , appears in bulk as an adherent powder. If allowed to fall from the side of the bottle, it retains the shape of the bottle, much as undried sea-sand does. If rubbed with the side of a knife it crunches, and the bright metallic scale so produced appears, on magnification, to have globules of mercury exuding from it. If pushed up into a fold of wash-leather with a tooth-brush handle, a large proportion of clean mercury globules can be pressed through the leather. When stirred into cedarwood oil and examined microscopically, it appears as crumbling, coherent, homogeneous masses, not separable into individual grains. The masses have no appearance of liquidity, their outlines are irregular and angular, especially the smaller detached particles, and the points tend to be blunt rather than spiky.

It is not proposed to continue this investigation, but Dr. J. C. Philip hopes to examine the physical properties of some of these amalgams, and to study the influence of the medium on the velocity of the reaction between mercuric halides and metallic silver.

ROYAL COLLEGE OF SCIENCE,
SOUTH KENSINGTON.

XXXVIII.—*Halogen Derivatives of Malonanilide, Ethyl Malonanilate, and Malonanilic Acid.*

by FREDERICK DANIEL CHATTAWAY and FREDERICK ALFRED MASON.

Compounds of this nature are at present almost unknown, although knowledge of their properties is necessary before the action of halogens on the parent substances can be followed and before one of the least studied cases of intramolecular rearrangement can be further investigated.

The scanty literature dealing with the subject leaves the impression that compounds of this class are difficult to prepare by direct method, whereas the exact reverse is the case.

The halogen derivatives of malonanilide and of ethyl

malonanilate are produced together when malonic ester in some excess is heated for a short time with the corresponding aniline, and can easily be separated, owing to the sparing solubility of the anilides in all ordinary solvents. The best results are obtained when about one gram-molecule of the aniline and one and a-half gram-molecules of malonic ester are employed; if less ester is used, some aniline, which is troublesome to remove by crystallisation, is left, whilst if more ester is taken, the products remain partly dissolved in the excess which has to be distilled off, a brownish-coloured product, which needs much purification, being obtained. About 10 to 15 grams of aniline is a convenient amount to use in one operation.

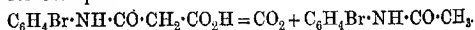
The aniline and ester are heated together in a flask attached to a long tube, which serves as a condenser, and the rate of boiling of the mixture is regulated so that the alcohol formed mainly escapes while the malonic ester is returned to the flask.

The yields are generally good, no appreciable decomposition occurring, the loss arising only from the necessary separation and purification.

The halogen-substituted malonanilic acids are also very easily obtained by hydrolysing the substituted malonanilic esters: the crude products from which the substituted malonanilides have been separated suffice for this purpose.

The esters can be hydrolysed by heating for a short time with aqueous sodium or potassium hydroxide, or even by heating for a longer time with water alone, but it is preferable to suspend them in a dilute solution of sodium carbonate and to pass steam through the liquid until the ester disappears. This method has the advantage that if any aniline remains admixed with the crude ester or is formed during hydrolysis, it passes over with the steam. The acid is separated from the sodium salt in a crystalline state, after concentrating the solution if necessary, by adding a slight excess of hydrochloric acid.

When heated, the malonanilic acids decompose quantitatively into carbon dioxide and the corresponding substituted acetanilide, thus; for example:



EXPERIMENTAL.

pp-Dichloromalonanilide, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$

This compound, together with ethyl *p*-chloromalonanilate, is produced when *p*-chloroaniline is heated with ethyl malonate. A mixture of 12 grams of *p*-chloroaniline and 25 grams of ethyl

MALONANILIDE, ETHYL MALONANILATE, AND MALONANILIC ACID 341

malonate, was stirred for thirty minutes, the alcohol formed being allowed to escape. The semi-solid mass left on cooling was shaken with four times its bulk of alcohol, and the dichloromalonanilide which remained undissolved was collected and recrystallised alternately from alcohol and acetic acid. It is fairly soluble in boiling alcohol or acetic acid, and separates from either in small, slender, colourless needles, which, when dry, form a felted mass. The yield of pure product obtained thus is about 20 per cent. of the theoretical yield from the amount of aniline used.

pp-Dichloromalonanilide melts and decomposes at 261° :

0.2474 gave 0.2206 AgCl. Cl = 22.06.

$C_{15}H_{12}O_2N_2Cl_2$ requires Cl = 21.95 per cent.

Ethyl p-Chloromalonanilate, $C_6H_4Cl \cdot NH \cdot CO \cdot CH_2 \cdot CO_2 \cdot C_2H_5$.

This compound was obtained as a white, crystalline powder by slowly adding water to the filtrate from which dichloromalonanilide had been separated. It was purified by repeatedly crystallising it from hot alcohol, in which it is very easily soluble, and from which it separates in short, colourless prisms, melting at 97° . It is very readily soluble in all common organic solvents, but only very sparingly so in water:

0.2146 gave 0.1285 AgCl. Cl = 14.81.

$C_{11}H_{12}O_3NCl$ requires Cl = 14.68 per cent.

p-Chloromalonanilic Acid, $C_6H_4Cl \cdot NH \cdot CO \cdot CH_2 \cdot CO_2H$.

This compound was prepared by suspending ethyl *p*-chloromalonanilate in twenty times its weight of water containing rather more than the equivalent amount of sodium carbonate and passing steam through the liquid until the ester had disappeared. On adding hydrochloric acid in slight excess to the cooled product, the acid separated in thin, colourless plates. It was purified by recrystallisation either from hot water, in which it is moderately soluble, or from hot alcohol, in which it is readily so. It separates from either solvent in glistening, colourless, flattened prisms or plates. On heating, it melts and decomposes, and evolves carbon dioxide at about 168° ,* leaving a residue of pure *p*-chloroacetanilide, which, after solidification, re-melts at 175° :

* The melting points of this and the other substituted malonanilic acids described in the paper represent the temperatures at which the substances melt and rapidly decompose with gas evolution when quickly heated. The temperatures at which this melting takes place vary considerably with the rate of heating. Decomposition runs to some extent before these temperatures are reached, and if the acids are only heated, they appear to melt at lower temperatures.

Ethyl p-Bromomalonanilate, $C_6H_4Br \cdot NH \cdot CO \cdot CH_2 \cdot CO_2 \cdot C_2H_5$

Ethyl *p*-bromomalonanilate crystallises from alcohol, in which it is easily soluble, in colourless, short, rhombic prisms, melting at 99°. 0.2715 gave 0.1788 AgBr. Br=28.03.

$C_{11}H_{12}O_3NBr$ requires Br=27.94 per cent.

p-Bromomalonanilic Acid, $C_6H_4Br \cdot NH \cdot CO \cdot CH_2 \cdot CO_2H$

This compound is sparingly soluble in boiling water, but readily so in hot alcohol. It crystallises from water or alcohol in colourless, flattened, slender prisms. It melts at 169°, carbon dioxide is evolved, and *p*-bromoacetanilide is formed:

0.1750 gave 0.1271 AgBr. Br=30.91.

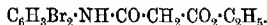
$C_8H_8O_3NBr$ requires Br=30.98 per cent.

2:4:2':4'-Tetrabromomalonanilide,

This compound crystallises from boiling acetic acid, in which it is moderately soluble, in colourless, long, flattened needles or prisms, melting at 233°:

0.2092 gave 0.2769 AgBr. Br=56.33.

$C_{15}H_{10}O_2N_2Br_4$ requires Br=56.11 per cent.

Ethyl 2:4-Dibromomalonanilate,

This compound crystallises from alcohol, in which it is easily soluble, in colourless, slender, flattened prisms, melting at 86°:

0.2431 gave 0.2496 AgBr. Br=43.69.

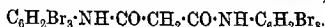
$C_{11}H_{11}O_3NBr_2$ requires Br=43.80 per cent.

2:4-Dibromomalonanilic Acid, $C_6H_3Br_2 \cdot NH \cdot CO \cdot CH_2 \cdot CO_2H$

2:4-Dibromomalonanilic acid is sparingly soluble in water, but easily so in alcohol. It crystallises from alcohol in colourless, flattened prisms. When heated, it melts, and evolves carbon dioxide at 174°, 2:4-dibromoacetanilide being formed:

0.2880 gave 0.3195 AgBr. Br=47.21.

$C_8H_7O_3NBr_2$ requires Br=47.44 per cent.

2:4:6:2':4':6'-Hexabromomalonanilide,

This anilide is so sparingly soluble in all ordinary solvents that it can only be recrystallised in very small amount from boiling acetic acid. A few tenths of a gram only are dissolved by a litre

of boiling. It is soluble in many organic solvents in colourless, very small, hair-like needles. It can be recrystallised from boiling nitrobenzene, but the product obtained is not quite pure, and very considerable loss from decomposition occurs. It melts and evolves gas at 331° :

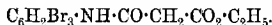
0.1314 gave 0.2041 AgBr. Br = 66.10.

$C_{15}H_{18}O_2N_2Br_6$ requires Br = 65.90 per cent.

Freund (*Ber.*, 1884, 17, 782) obtained a compound to which he assigned this constitution by dissolving malonanilide in glacial acetic acid, and adding bromine in slight excess to the warmed solution drop by drop. The liquid on cooling deposited a thick crop of needles, which, after several recrystallisations from acetic acid, melted at $145-146^{\circ}$. This substance, on heating in a sealed tube with fuming hydrochloric acid at 200° , yielded a compound which he regarded as symmetrical tribromoaniline, and from this observation he deduced its constitution.

Freund's compound, however, differs so entirely in its properties from the compound described above, which itself possesses all the properties that would be expected from a consideration of those of the other members of the class described in this paper, that it cannot have the constitution assigned by him to it.

Ethyl 2:4:6-Tribromomalonanilate,



Ethyl 2:4:6-tribromomalonanilate is readily soluble in hot alcohol, and crystallises from it in colourless, slender prisms, melting at 177° :

0.1458 gave 0.1854 AgBr. Br = 54.11.

$C_{11}H_{10}O_3NBr_3$ requires Br = 54.02 per cent.

2:4:6-Tribromomalonanilic Acid, $C_6H_2Br_3 \cdot NH \cdot CO \cdot CH_2 \cdot CO_2H$.

2:4:6-Tribromomalonanilic acid crystallises from alcohol, in which it is moderately soluble, in small, colourless needles. If the acid is rapidly heated, it melts and evolves carbon dioxide at about 201° , 2:4:6-tribromoacetanilide being produced. If slowly heated, however, it decomposes below this temperature without melting, carbon dioxide as before is given off, whilst 2:4:6-tribromoacetanilide, which, if the temperature be raised, melts sharply at 232° , is left in the tube:

0.2000 gave 0.2699 AgBr. Br = 57.43.

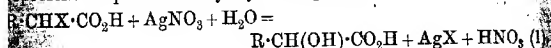
$C_{11}H_6O_3NBr_3$ requires Br = 57.66 per cent.

UNIVERSITY CHEMICAL LABORATORY,
OXFORD.

Reactivity of the Halogens in Organic Compounds. Part IV. Interaction of Bromoacetic, Bromopropionic, and α -Bromobutyric Acids and their Sodium Salts with Silver Salts in Aqueous Solution. Catalytic Action of Silver Halides.

By GEORGE SEETER.

In previous papers (Trans., 1907, **91**, 460; Proc., 1908, **24**, 89; *Festschrift Jubelband*, 1910, II, 511; Trans., 1909, **95**, 1827) the results of an experimental investigation of the rate of displacement of the halogens in the lower members of the series of halogen substituted fatty acids have been communicated, and the mechanism of the respective reactions has been discussed. The present paper deals mainly with the interaction of the first three members of the series of α -bromo-fatty acids and their sodium salts with silver nitrate and silver acetate in dilute aqueous solution. It was shown many years ago by Beckurts and Oddo (*Ber.*, 1881, **14**, 576; 1883, **16**, 222) that the reaction between silver nitrate and the lower members of the series of bromo-fatty acids in aqueous solution is represented quantitatively by the equation:



in which R represents hydrogen or an alkyl group, and X a halogen atom.

In the course of the present investigations, the remarkable observation was made that reactions of the above type are very markedly accelerated by silver bromide; even when the solution is only 1/300 molar with reference to silver bromide (which is, of course, mainly present in the insoluble form), the rate of the reaction may be doubled or even trebled. This action appears to account for a number of hitherto unexplained observations made by previous investigators.

The other more important results of the investigation are that the rate of reaction increases very considerably with the increase in complexity of the alkyl group R, and that the sodium salts react more rapidly than the free acids. Nitric acid exerts a very powerful retarding effect on the reactions in which silver nitrate is concerned. Silver acetate reacts with the bromo-fatty acids more rapidly than does silver nitrate under equivalent conditions.

Method of measurement.—The reacting substances were mixed at instant temperature in small tubes of Jena glass, which were then corked and kept in a thermostat at a temperature kept constant to within 0.1° . At definite intervals the contents of a tube were poured into a slight excess of a $N/50$ -solution of ammonium thiocyanate, which at once stopped the reaction, 5 c.c. of a concentrated solution of iron alum and 5 c.c. of concentrated nitric acid, free from nitrous fumes, were then added, and the excess of thiocyanate estimated by titrating with $N/50$ -silver nitrate.

It is known that the above method of titration does not give accurate results for chlorides, owing to the solubility of the precipitated silver chloride in ammonium thiocyanate. Theoretically, however, there should be no appreciable error in the case of bromides, owing to the much smaller solubility of silver bromide, and this conclusion has been confirmed experimentally by Rosanoff and Hill (*J. Amer. Chem. Soc.*, 1907, **29**, 1467). In order to ensure that no error arises in the present case owing to the presence of precipitated silver bromide, the method of titration described above has been tested in various ways, and has been found to give quite accurate results.

The tubes in which the reactions were carried out held about 15 c.c., and in all cases the reaction mixture measured 12 c.c. The titration values quoted in the tables are throughout (except in table I) the mean of two simultaneous experiments. The measurements were made at 26.0° .

Reaction between α -Bromopropionic Acid and Silver Nitrate.

The results of a typical series of experiments with α -bromopropionic acid and silver nitrate are quoted in table I. The unit of concentration is the amount of silver nitrate contained in 1 c.c. of a $N/50$ -solution of the salt, and the concentration of the halogen fatty acids (and their sodium salts) is expressed in equivalent units in accordance with the experimental fact that $R\cdot CHBr\cdot CO_2H$ (and $R\cdot CHBr\cdot CO_2Na$) is equivalent to $AgNO_3$. The constants in the last column are calculated according to the equation for a reaction of the second order:

$$k = \frac{1}{t} \frac{x}{a(a-x)}$$

when the reacting substances are present in equivalent amounts. In all cases, $a-x$ in the tables represents the concentration of the

silver nitrate at the time t is $a - x$, the concentration of α -bromopropionic acid actually estimated is $b(a - x)$.

If it is desired to refer k , the velocity-coefficient or velocity constant of the reaction, to a concentration of 1 mol. per litre, the values of k given in the tables must be multiplied by $12 \times 50 = 600$, since the values quoted are obtained by titrating 12 c.c. of the reaction mixture with 1/50 molar thiocyanate.

Throughout this paper, the concentrations given refer to the reaction mixture; thus, in the experiments quoted in table I, the reaction mixture was initially $N/30$ with reference to both the reacting substances.

TABLE I.

Silver nitrate, $N/30$. α -Bromopropionic acid, $N/30$.

t (min.).	$a - x$.	k .	$a - x$.	k .
0	20.0	—	20.0	—
10	18.1	0.00050	18.0	0.00056
30	14.7	0.00060	14.7	0.00060
90	10.2	0.00058	10.0	0.00056

These figures show that the results of parallel experiments are in good agreement, and the fair agreement of the velocity-coefficients in the course of a reaction is in accord with the assumption that the reaction is bimolecular. It will be shown in the sequel, however, that the latter result is only attained owing to a combination of two factors which influence the reaction in opposite directions.

It is well known that one of the best methods of deciding the "order" of a reaction is to measure its velocity with varying initial concentrations; in this way disturbances arising in the course of the reaction are to a great extent eliminated. The results for the reaction under discussion are given in table II, the values of k , when the concentrations are not equivalent, being calculated by the general formula for a bimolecular reaction:

$$0.4343 k = \frac{1}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)},$$

where the symbols have the usual significance.

TABLE II.

Concentration of silver nitrate.	Concentration of α -bromopropionic acid.	k .
$N/10$	$N/40$	0.00047
$N/20$	$N/40$	0.00059
$N/40$	$N/40$	0.00054
$N/20$	$N/20$	0.00053
$N/20$	$N/10$	0.00051

The above results appear to show that, in spite of certain irregularities, the rate of the reaction is in the first instance

proportion to the initial concentration of the reacting substances through a range of concentration from $N/10$ to $N/40$ in each case.

It was soon noticed that when the aqueous solution of the acid was not freshly prepared, the reaction was considerably more rapid. This is illustrated by the results quoted in the accompanying table.

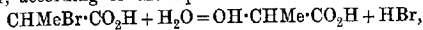
TABLE III.

Silver nitrate and bromopropionic acid, each $N/30$.

(Acid solution, two hours old.)			(Acid solution, kept two days at 26°.)		
<i>t</i> (min.).	<i>a</i> - <i>z</i> .	<i>k</i> .	<i>t</i> (min.).	<i>a</i> - <i>z</i> .	<i>k</i> .
0	20.0	—	0	20.0	—
10	18.5	0.00041	10	16.4	0.00110
30	15.4	0.00050	30	12.0	0.00111
90	10.5	0.00050	90	8.3	0.00080

It is clear that the initial velocity is nearly three times as great when the acid solution is kept two days before the rate of reaction is measured.

It is well known that α -bromopropionic acid is slowly decomposed by water, according to the equation:



and in an earlier paper the results of an experimental investigation of this reaction have been communicated. A little hydrobromic acid is formed during the reaction, and at once reacts with part of the silver nitrate on mixing the reacting substances. As the speed of the reaction is deduced from the rate at which the silver nitrate is used up, the apparent speed in the presence of hydrobromic acid will be greater than the actual speed with which silver nitrate and α -bromopropionic acid react. In order to estimate the error thus caused, the rate of hydrolytic decomposition of bromopropionic acid at 26° has been measured at 26° with the following results (table IV). The concentrations of bromopropionic acid and of hydrobromic acid are expressed in terms of the number of c.c. of $N/20$ -sodium hydroxide required to neutralise 5 c.c. of the solution, which was approximately $N/5$:

TABLE IV.

Time (days).	Five c.c. of acid solution titrated.	Concentration of HBr formed.	
		In c.c. of $N/20$ -NaOH.	Normality.
0	19.70	0.00	—
3	20.10	0.40	0.001
6	20.35	0.65	0.0016
9	20.60	0.90	0.0023
12	20.80	1.10	0.0028

The reaction at 26° is therefore extremely slow, and the amount

of hydrobromic acid.

These results appear to be at least two plausible explanations of the results in question: (1) that the silver bromide formed in the course of the reaction exerts a catalytic influence; (2) that the bromopropionic acid in aqueous solution undergoes a slow change into a second more active modification. The first suggestion can be tested by adding some hydrobromic acid or potassium bromide to the bromopropionic acid before adding the silver nitrate. Some of the results obtained in this way are given in table V.

TABLE V.

Composition of Mixture I.				Composition of Mixture II.			
Bromopropionic acid, <i>N</i> /5 ...		2 c.c.		Bromopropionic acid, <i>N</i> /5 ...		2 c.c.	
Water		5 "		Potassium bromide, <i>N</i> /25		2 "	
Silver nitrate, <i>N</i> /12.5		5 "		Water		2 "	
Silver nitrate, <i>N</i> /12.5		5 "		Silver nitrate, <i>N</i> /12.5		6 "	
(min.)	$\alpha - \alpha$.	k .		t (min.)	$\alpha - \alpha$.	k .	
0	20.0	—		0	20.0	—	
10	18.5	0.00041		10	15.7	0.00137	
20	15.4	0.00050		20	13.3	0.00126	
30	10.5	0.00050		40	10.0	0.00125	

The data in the above table show that, after mixing, the two solutions are exactly equivalent in concentration; the only difference is that in the second mixture a small amount of silver bromide (and potassium nitrate) is present. The mixture is only 1/25 molar with respect to this salt, and doubtless the greater part of it is present in the insoluble form, yet the remarkable result is obtained that this trace of silver bromide more than trebles the initial speed of the main reaction. Moreover, this by no means represents the maximum catalytic power of the silver bromide, as the greater part of it coagulates and rises to the top of the solution soon after mixing the reagents.

Reference to the data in table III shows that the solution of bromopropionic acid, which had stood two days at 26°, cannot have been more than 1/1000 normal with reference to hydrobromic acid, so that the small amount of silver bromide formed by interaction of the acid with silver nitrate has a very powerful catalytic action.

The catalytic acceleration of reactions of this type by silver bromide and iodide is further referred to in a later part of the paper (pp. 357, 358).

(c) *Nitric Acid*.—Nitric acid, even in very dilute solution, very readily retards the reaction between silver nitrate and α -bromopropionic acid. Some of the results, typical of an extended series of experiments on this point, are given in the accompanying table.

• TABLE VI.

Silver nitrate, $N/20$. Bromopropionic acid, $N/20$.

No nitric acid.			Nitric acid, $N/80$.			Nitric acid, $N/15$.		
t	α -x.	k .	t	α -x.	k .	t	α -x.	k .
0	30.0	—	0	30.0	—	0	30.0	—
10	26.7	0.00041	20	28.0	0.000129	30	28.45	0.000089
30	21.5	0.00045	60	25.0	0.000111	60	25.75	0.000066

The figures show that in the presence of $N/15$ -nitric acid the rate of the reaction is diminished to about 1/7th of its original value.

(b) *Benzenesulphonic Acid*.—For comparison with nitric acid, some experiments were made with benzenesulphonic acid under the same conditions. It was found that the latter acid retards the reaction to a rather greater extent than nitric acid. The initial value of the constant in the presence of $N/15$ -benzenesulphonic acid is 0.000053, as compared with 0.000061 for $N/15$ -nitric acid.

It is probable that benzenesulphonic acid is a rather stronger acid than nitric acid, but the difference in the reactivities seems rather greater than can be accounted for on this basis.

(c) *Lactic Acid*.—As lactic acid is one of the products of the reaction, its influence on the velocity was measured with the following results:

TABLE VII.

Silver nitrate, $N/20$. Bromopropionic acid, $N/20$.

No lactic acid.			Lactic acid, $N/5$.		
t (min.).	α -x.	k .	t (min.).	α -x.	k .
0	30.0	—	0	30.0	—
10	26.1	0.00050	10	26.9	0.00036
30	20.4	0.00053	30	22.1	0.00040
60	14.9	0.00056	60	18.4	0.00036

(d) *Sodium Nitrate*.—The results of a series of observations with this salt are given in the accompanying table; much higher concentrations were used than in the case of the acids:

Silver nitrate, *N*/30. Bromopropionic acid, *N*/30.

<i>t</i> (min.).	No sodium nitrate.		Sodium nitrate, <i>m</i> /2.		Sodium nitrate, <i>m</i> /1.	
	<i>a</i> - <i>z</i> .	<i>k</i> .	<i>a</i> - <i>z</i> .	<i>k</i> .	<i>a</i> - <i>z</i> .	<i>k</i> .
0	20.0	—	20.0	—	20.0	—
10	17.9	0.00060	18.3	0.00045	18.7	0.00035
30	14.6	0.00062	15.7	0.00045	16.2	0.00039

The facts that nitric acid and benzenesulphonic acid, which are both highly ionised in solution, retard the reaction to about the same extent, and that the NO_3^- ion has only a very slight retarding action, indicate that the effect in question is mainly due to the H^+ ions. This is confirmed by the fact that lactic acid, which is a comparatively weak acid, has a very slight retarding action. The bearing of these results on the mechanism of the reaction is discussed later (p. 361).

Effect of Alcohol and of Acetone on the Rate of Reaction.

A few experiments were made in which half the water used as solvent was displaced by alcohol and by acetone respectively; the results were as follows:

TABLE IX.

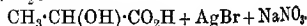
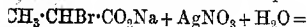
Silver nitrate, *N*/30. Bromopropionic acid, *N*/30.

<i>t</i> (min.).	Water.		Water + alcohol.		Water + acetone.	
	<i>a</i> - <i>z</i> .	<i>k</i> .	<i>a</i> - <i>z</i> .	<i>k</i> .	<i>a</i> - <i>z</i> .	<i>k</i> .
0	20.0	—	20.0	—	20.0	—
10	18.0	0.00056	17.5	0.00071	17.4	0.00073
30	14.6	0.00062	13.9	0.00073	14.3	0.00067

It is interesting to note how small an alteration is produced in the reaction velocity by the displacement of half the water by alcohol or by acetone. It has already been shown by Euler (*Ber.*, 1906, 39, 2726) that the rate of reaction between chloroacetic acid and silver nitrate is approximately the same in water and in 45 per cent. alcohol.

Sodium Bromopropionate and Silver Nitrate.

The reaction in this case is represented by the equation:



The sodium bromopropionate was prepared just before the reaction by careful neutralisation of a solution of bromopropionic acid with sodium hydroxide. The results of one series of experi-

ments, in the case of the reaction of the acid and its sodium salt are given in the accompanying table:

TABLE X.

Silver nitrate, <i>N</i> /80. Bromopropionic acid, <i>N</i> /80.			Silver nitrate, <i>N</i> /80. Sodium bromopropionate, <i>N</i> /80.		
<i>t</i> (min.).	<i>a</i> - <i>x</i> .	<i>k</i> .	<i>t</i> (min.).	<i>a</i> - <i>x</i> .	<i>k</i> .
0	20.0	—	0	20.0	—
10	18.0	0.00056	5	16.6	0.0020
30	14.7	0.00060	15	11.0	0.0027
90	10.2	0.00054	45	6.4	0.0024

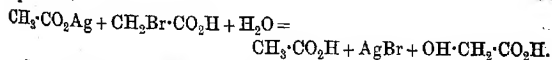
The velocity-coefficients, *k*₁, for a bimolecular reaction in the case of the sodium salt are only in moderate agreement, a result which is doubtless to be anticipated. The initial velocity is about four times that obtained for the free acid. The considerable increase of the coefficient between five and fifteen minutes is no doubt due to the catalytic influence of silver bromide. A few measurements were also made to determine the influence of the initial concentration on the reaction velocity, with the following results:

	<i>k</i> .
Sodium bromopropionate, <i>N</i> /80	} 0.0020
Silver nitrate, <i>N</i> /30	
Sodium bromopropionate, <i>N</i> /60	} 0.0030
Silver nitrate, <i>N</i> /60	

showing that the initial velocity is the greater the more dilute the solution.

Bromopropionic Acid and Silver Acetate.

If the conclusion drawn from the experiments already described—that silver bromide exerts a catalytic influence on the rate of reaction—is valid, the velocity-coefficients calculated for a reaction of the second order ought regularly to increase, owing to the increase in the amount of silver bromide as the reaction proceeds. However, nitric acid, another product of the reaction, exerts a retarding influence, and the result of these two effects is that in many cases the reactions follow the law for a bimolecular reaction fairly accurately. In order to eliminate the retarding influence of nitric acid, it was considered desirable to perform a few experiments with the silver salt of a weak acid, and for this purpose silver acetate was chosen. The reaction in this case is represented by the equation:



Some typical results are quoted in table XI:

*Fresh Bromopropionic Acid*Silver acetate, *N*/30.
Bromopropionic acid, *N*/30.

<i>t</i> (min.)	<i>a</i> - <i>x</i> .	<i>k</i> .
0	20.0	—
5	18.2	0.00100
15	14.0	0.00143
30	9.5	0.00186

Silver acetate, *N*/100.
Bromopropionic acid, *N*/30.

<i>t</i> (min.)	<i>a</i> - <i>x</i> .	<i>k</i> .
0	6.0	—
10	4.75	0.00130
30	2.75	0.00148
60	0.70	0.00186

*Bromopropionic Acid (kept two days at 26°).*Silver acetate, *N*/30.
Bromopropionic acid, *N*/30.

<i>t</i> (min.)	<i>a</i> - <i>x</i> .	<i>k</i> .
0	20.0	—
5	16.8	0.00200
15	10.5	0.00307
30	7.6	(0.00272)

Silver acetate, *N*/30.
Bromopropionic acid, *N*/30.

<i>t</i> (min.)	<i>a</i> - <i>x</i> .	<i>k</i> .
0	20.0	—
10	16.5	0.00250
30	12.8	0.00327

It will be observed that in all these experiments the velocity coefficients calculated for a reaction of the second order increase very considerably during the reaction, doubtless owing to the catalytic influence of the silver bromide. The same effect is seen in the solution which has been kept two days, and in which, therefore, a little hydrobromic acid has been formed. The very small amount of silver bromide produced as soon as the two solutions are mixed is sufficient to double the initial speed of the reaction. This catalytic effect is also illustrated in the following table; in one case a small amount of potassium bromide is added to the acid before mixing:

TABLE XII.

Silver acetate, <i>N</i> /25	8 c.c.	Silver acetate, <i>N</i> /25	9 c.c.		
Bromopropionic acid, <i>N</i> /6.25 ..	2 "	Bromopropionic acid, <i>N</i> /6.25 ..	2 "		
Water	2 "	Potassium bromide, <i>N</i> /25	1 "		
<i>t</i> (min.)	<i>a</i> - <i>x</i> .	<i>k</i> .	<i>t</i> (min.)	<i>a</i> - <i>x</i> .	<i>k</i> .
0	16.00	—	0	16.00	—
5	14.20	0.00158	5	11.30	0.00520
10	12.40	0.00181	10	9.80	0.00395
20	9.65	0.00206	20	7.00	0.00402
30	7.00	0.00268			

These results indicate that 1/300 molar silver bromide more than trebles the initial speed of the reaction, but that the velocity falls off somewhat as the reaction proceeds. This is doubtless connected with the fact that the greater part of the silver bromide soon coagulates, and rises to the top of the solution; it can then exert no catalytic influence.

Relative Velocities with Silver Nitrate and Silver Acetate.

Simultaneous measurements were made with silver nitrate and silver acetate in equivalent concentration, in order to obtain an accurate record of their relative activities with bromopropionic acid. The results are as follows:

TABLE XIII.

Silver nitrate, N/30. Bromopropionic acid, N/30.			Silver acetate, N/30. Bromopropionic acid, N/30.		
t (min.).	a - x.	k.	t (min.).	a - x.	k.
0	20.0	—	0	20.0	—
10	17.8	0.00062	5	17.9	0.00120
30	14.2	0.00063	17	12.6	0.00170
90	9.5	0.00061	45	6.6	0.00220

It follows that the initial velocity with the nitrate is about half that with the acetate under corresponding conditions. The bearing of this result on the mechanism of the reaction is considered later.

Reaction between α-Bromobutyric Acid and Silver Nitrate.

Corresponding measurements to those just described for bromopropionic acid have been made with bromobutyric acid, but not in the same detail. The reaction is represented by the equation:
 $\text{CH}_3\text{Br}\cdot\text{CO}_2\text{H} + \text{AgNO}_3 + \text{H}_2\text{O} = \text{OH}\cdot\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H} + \text{AgBr} + \text{HNO}_3$

The results are similar to those obtained for bromopropionic acid, except that the velocity-coefficients diminish more rapidly during the reaction. The data for experiments in which the initial concentrations were varied are given in table XIV, the initial values of the velocity-coefficients being given in the third column:

TABLE XIV.

Concentration of silver nitrate.	Concentration of bromobutyric acid.	k.
N/60	N/60	0.0060
N/40	N/40	0.0034
N/20	N/40	0.0021
N/10	N/40	0.0014
N/40	N/20	0.0034
N/40	N/10	0.0028

It is clear from these results that when the concentration of silver nitrate is kept constant, and that of the bromopropionic acid varied, there is not much alteration in the magnitude of the velocity-coefficients; in other words, the rate of the reaction is approximately proportional to the concentration of the bromobutyric acid. On the other hand, the coefficients diminish considerably as the initial concentration of silver nitrate is increased, which indicates that when the silver nitrate concentration is increased, the rate of the reaction does not increase in the same proportion. This does not correspond with the behaviour of silver

nitrate and α -bromopropionic acid, the velocity coefficients retain approximately the same value with varying concentration (p. 348).

Effect of Nitric Acid.—The actual observations are quoted in this case, as they illustrate very clearly the falling off in the magnitude of the velocity coefficients as the reaction progresses:

TABLE XV.

Silver nitrate, $N/20$. - Bromobutyric acid, $N/20$.

No nitric acid.			Nitric acid, $N/15$.			Nitric acid, $N/7.5$.		
t (min.).	$a-x$.	k .	t (min.).	$a-x$.	k .	t (min.).	$a-x$.	k .
0	30.0	—	0	30.0	—	0	30.0	—
5	23.4	0.0019	15	24.6	0.00048	30	25.3	0.00020
15	18.8	0.0013	45	21.5	0.00029	90	22.6	0.00012

These results show that the retarding effect of nitric acid is considerable, and is approximately proportional to the concentration of the acid.

Sodium Bromobutyrate and Silver Nitrate.—The magnitude of the constant in $1/30$ molar solution of each of the reacting substances is 0.0060. The speed is therefore about 2.5 times that with the free acid, for which the constant is about 0.0024.

Bromoacetic Acid and Silver Nitrate.

As this reaction has already been investigated to some extent by Euler (*loc. cit.*), it has been considered sufficient for the present purpose to make a few measurements with the object of comparing this acid with the two higher acids as regards its reactivity with silver nitrate, and, further, to determine if this reaction, like the others, is catalytically accelerated by silver bromide. The results are given in table XVI:

TABLE XVI.

Silver nitrate, $N/12.5$	5 c.c.	Silver nitrate, $N/12.5$	6 c.c.		
Bromoacetic acid, $N/5$	2 "	Bromoacetic acid, $N/5$	2 "		
Water	5 "	Potassium bromide, $N/25$	2 "		
		Water	2 "		
t (min.).	$a-x$.	k .	t (min.).	$a-x$.	k .
0	20.0	—	0	20.0	—
240	19.5	0.0000048	180	18.1	0.000029
1200	17.6	0.0000057	1200	11.6	0.000050
2760	13.4	0.0000089	2760	9.6	0.000023

The data quoted in the table show that the rate of reaction between silver nitrate and bromoacetic acid is very slow at 26 the rate is only about $1/100$ th of the corresponding reaction with bromopropionic acid. Further, silver bromide greatly accelerates

the reaction was about six times that in the absence of the silver bromide.

Sodium Bromoacetate and Silver Nitrate.—The results given in table XVII show that sodium bromoacetate reacts with silver nitrate about three times as rapidly as does the free acid.

TABLE XVII.

Bromoacetic acid, <i>N</i> /80. Silver nitrate, <i>N</i> /30.			Sodium bromoacetate, <i>N</i> /30. Silver nitrate, <i>N</i> /30.		
<i>t</i> (min.).	α -z.	<i>k</i> .	<i>t</i> (min.).	α -z.	<i>k</i> .
0	20.0	—	0	20.0	—
240	19.5	0.0000054	240	18.6	0.000016
1200	17.2	0.0000068	1200	13.2	0.000021
2760	13.8	0.0000081	2760	7.4	0.000031

Methyl Iodide and Silver Nitrate.

As this reaction has been measured by several previous observers, who, however, did not detect the catalytic influence of the silver iodide, it has been considered desirable to repeat the measurements, with special reference to the effect of silver iodide in aqueous solution. Some typical results are given in the accompanying table:

TABLE XVIII.

Solvent: Water.

I.			II.		
Silver nitrate, <i>N</i> /20..... 5 c.c.			Silver nitrate, <i>N</i> /20 6 c.c.		
Methyl iodide, <i>N</i> /20 ... 5 "			Methyl iodide, <i>N</i> /20 5 "		
Water..... 2 "			Potassium iodide, <i>N</i> /20..... 1 "		
<i>t</i> (min.).	α -z.	<i>k</i> .	<i>t</i> (min.).	α -z.	<i>k</i> .
0	12.50	—	0	12.50	—
15	11.60	0.00042	15	10.70	0.00080
30	10.95	0.00039	30	9.65	0.00078
60	9.70	0.00039	60	8.00	0.00075
120	8.30	0.00034	120	6.70	0.00058
180	6.80	0.00037	180	5.10	0.00065

Solvent: Alcohol.

III (composition as I).			IV (composition as II).		
<i>t</i> (min.).	α -z.	<i>k</i> .	<i>t</i> (min.).	α -z.	<i>k</i> .
0	12.5	—	0	12.5	—
10	10.75	0.00180	10	10.4	0.00162
30	8.50	0.00126	30	8.3	0.00135
60	6.73	0.00116	60	6.4	0.00127
120	4.90	0.00104	120	4.5	0.00119

These results show that the reaction in aqueous solution is considerably accelerated by *N*/240-silver iodide, and there appears to

be a corresponding, but much smaller, acceleration in alcoholic solution. The latter result, however, is of a preliminary nature, as only one series of measurements was made in alcohol.

In all these cases it has to be remembered that the amount of silver iodide distributed through the solution is only a small fraction of the total amount, as the precipitate, especially in alcoholic solution, soon coagulates, and then rises to the top or sinks to the bottom of the solution, being thus to a great extent removed from the sphere of action.

In experiments III and IV, besides silver iodide, a little potassium nitrate (1/240 molar) is formed on mixing the solutions. Direct experiment shows, however, that even in 1/20 molar solution potassium nitrate exerts no appreciable influence on the rate of the reaction in aqueous solution, and the same may safely be assumed as to its effect in alcoholic solution in so small concentration.

According to the above table, the rate in ethyl alcohol is to the rate in water as 3:1, a result not in satisfactory agreement with the recent measurements of Burke and Donnan (*Zeitsch. physikal. Chem.*, 1909, **69**, 148), who find the ratio to be about 6:1.

DISCUSSION OF RESULTS.

(1) *The Catalytic Influence of Silver Halogen Salts.*—In the previous pages it has been shown that silver bromide and silver iodide, even in extremely small concentration, exert a marked accelerating effect on reactions in which silver salts and halogen compounds are concerned. The conclusions drawn by previous observers as to the mechanism of such reactions require revision in the light of this observation.

The magnitude of the effect under favourable conditions is shown by the fact that 1/1000 molar silver bromide (about 0.002 gram in 12 c.c. of the reaction mixture) doubles the initial rate of reaction between silver nitrate and bromopropionic acid. Unfortunately, an accurate investigation of this effect is rendered very difficult by the fact already mentioned, that the precipitate soon coagulates and is withdrawn from the sphere of action by rising to the top or sinking to the bottom of the solution.

In order to find whether the catalytic influence pertained to the halogen compound in all forms, about 0.1 gram of freshly precipitated and carefully washed silver iodide was added to a mixture of silver nitrate and methyl iodide, and the rate of the reaction measured. The mean value of the velocity-coefficient in the presence of the added iodide was 0.00041, in its absence 0.00035, a comparatively small acceleration. The data quoted in table

XVIII show that 1/8th of this amount of iodide, precipitated in the reaction mixture, produces a much greater acceleration.

It seems probable, therefore, that the catalytic power is connected with the fineness of division of the silver iodide, possibly with its occurrence in the colloidal (hydrosol) form. Lottermoser and Rothe (*Zeitsch. physikal. Chem.*, 1908, **62**, 359) have shown that silver iodide hydrosol is much less stable when the silver nitrate is in excess than when excess of potassium iodide is present. As the silver salt is necessarily in excess in the reactions now under investigation, the comparatively rapid coagulation of the precipitate is accounted for. The view that the acceleration is connected with the colloidal form of the silver iodide appears to be supported by the observation that the catalytic effect is much smaller in alcoholic solution, in which the hydrosol appears to be less stable.

These observations are interesting also in connexion with the experiments of Miss Burke and Donnan on the reaction between the alkyl halides and silver nitrate in alcoholic solution. They found that whilst the velocity-coefficients calculated for a reaction of the second order remained more or less constant with variation of the initial concentration of the alkyl iodide, they increased with increasing concentration of the silver nitrate. In other words, if we consider a reaction-mixture originally $N/20$ with regard to both components, at the moment when the concentration has fallen to $N/40$, the reaction is found to be proceeding more rapidly than in a solution in which the reacting substances are originally $N/40$. In spite of a very detailed investigation, the results of which have just been published (*Zeitsch. physikal. Chem.*, 1909, **69**, 148), the authors have obtained no satisfactory explanation of this phenomenon, although they favour the suggestion of Wegscheider and Frankl (*Monatsh.*, 1907, **28**, 91) that it is the non-ionised silver nitrate which enters into reaction.

It is evident, however, that the results could be at once accounted for if silver iodide exerts a catalytic action in alcoholic solution, as it has been proved to do in aqueous solution in the present paper. The experiments in alcoholic solution quoted in table XVIII are, as already mentioned, of a preliminary character, and the matter is now being further investigated by Miss Burke. If the above explanation proves tenable, there will no longer be any experimental justification for Wegscheider's suggestion (*loc. cit.*) that it is the non-ionised silver nitrate which reacts.

(2) *The Mechanism of the Reactions.*—The mechanism of these reactions appears to be rather complicated, and the full discussion is postponed until the results of further investigations are available, more particularly the rate of reaction of the halogen-substituted

esters with silver nitrate in the $N/30$ solution will be sufficient for our present purpose to summarise the more important results communicated in this paper which have a bearing on the mechanism of the reactions. Reactions of this type have often been discussed by previous observers, but no very definite conclusions as to their mechanism have been drawn. All that can be said with certainty is that the relatively great velocity is conditioned in some way by the tendency to formation of the halogen silver salts (compare Euler, *Ber.*, 1906, **39**, 2726; Wegscheider, *Monatsh.*, 1907, **28**, 79). In this connexion it is interesting to note that definite compounds of silver nitrate with certain organic halogen compounds (for example, $\text{AgNO}_3 \cdot \text{CH}_2\text{I} \cdot \text{CN}$ and $\text{AgNO}_3 \cdot \text{CH}_2\text{I}_2$) have been prepared by Scholl and Steinkopf (*Ber.*, 1906, **39**, 4393).

The fact that silver bromide and iodide exerts a catalytic effect on the reactions renders the interpretation of the results somewhat difficult, as we are not entitled to assume that the observed velocities are proportional to the intrinsic velocities. Pending further investigation, however, it may be assumed that the nearest approach to the relative intrinsic velocities is obtained by taking the initial velocities of the respective reactions.

It has already been pointed out that as regards compounds of the type $\text{R} \cdot \text{CHBr} \cdot \text{CO}_2\text{H}$ and their sodium salts, the velocity increases greatly with the complexity of the substituting group R. Under corresponding conditions, the relative reactivities of the first three acids and their sodium salts with silver nitrate are as follows:

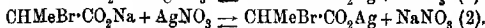
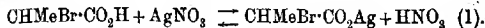
$\text{CH}_3\text{Br} \cdot \text{CO}_2\text{H}$ 0.0000955 [1]	$\text{CHMeBr} \cdot \text{CO}_2\text{H}$ 0.00055 [100]	$\text{CHEtBr} \cdot \text{CO}_2\text{H}$ 0.0025 [450]
$\text{CH}_3\text{Br} \cdot \text{CO}_2\text{Na}$ 0.000016 [4]	$\text{CHMeBr} \cdot \text{CO}_2\text{Na}$ 0.0025 [450]	$\text{CHEtBr} \cdot \text{CO}_2\text{Na}$ 0.0060 [1100]

The numbers in brackets give the relative reactivities of the compounds referred to the slowest as unity. The relative velocities depend to some extent on the concentrations for which the measurements are made—the above values are valid for $N/30$ solutions of the reacting substances.

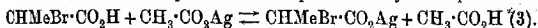
The velocities of these reactions have already been compared with those in which the halogen has been displaced in the presence of water alone, and when the sodium salts are acted on by alkali, and it has been pointed out that the reactions in which silver salts are employed are much more rapid. The reactions now under consideration also differ from those described in the previous papers as regards the magnitude of the difference in the reactivities. It is not usually considered that the substitution of a methyl group

for hydrolysis. The very marked difference in the reactivity of adjacent bromines, and yet bromopropionic acid is a hundred times more active than bromoacetic acid as regards silver nitrate. It is hoped that measurements with the corresponding esters will throw some light on the causes of this remarkable difference.

The fact that the sodium salts of the bromo-fatty acids react more rapidly than the free acids with silver nitrate is doubtless connected with the fact that the concentration of silver salt is higher in the former solutions than in the latter. The equilibria in the case of bromopropionic acid are represented by the equations:



As bromopropionic acid is a relatively weak acid, the equilibrium for reaction (1) will be displaced towards the right to a smaller extent than in equation (2), and therefore the concentration of silver bromopropionate—perhaps the substance which really reacts—will be smaller in the former case than in the latter. Similar considerations account for the fact that the initial rate of reaction of silver acetate is greater than that of silver nitrate (p. 355). In the former case, the equilibrium is represented by the equation:



and owing to the fact that acetic acid is a much weaker acid than bromopropionic acid, the equilibrium will be displaced towards the right, and the concentration of silver bromopropionate will be relatively great.

Another way of interpreting these results is to assume that it is the $\text{CHMeBr}\cdot\text{COO}'$ ion which reacts with silver nitrate. It can easily be calculated that the ratio of the $\text{CHMeBr}\cdot\text{COO}'$ ion concentration in sodium bromopropionate and bromopropionic acid in *N*/30 solution is about 4.5:1, which approximates to the ratio of their reactivities with silver nitrate. Similarly, the $\text{CH}_2\text{Br}\cdot\text{COO}'$ ion concentration in sodium bromoacetate and the free acid is about 4:1, whilst the ratio of their reactivities with silver nitrate is about 3:1.

The suggestion that it is mainly the ions of the bromo-fatty acids which react with silver nitrate is further supported by the experiments with nitric acid (p. 351). It can readily be calculated that the $\text{CHMeBr}\cdot\text{COO}'$ ion concentration in *N*/20-bromopropionic acid is reduced to about 1/7th of its value by the addition of *N*/15-nitric acid, which is just the ratio in which the reactivity of bromopropionic acid towards silver nitrate is reduced by the same proportion of nitric acid.

The fact that the rate of reaction is approximately proportional

to the concentration of the bromopropionic acid instead of to the square root of the concentration (p. 348) appears at first sight to be opposed to the view that the ions are the active agents, but this may be due to complications arising from the catalytic influence of the silver bromide.

There is no conclusive evidence as to what function of the silver nitrate is concerned in these reactions, but the fact that sodium nitrate retards the reaction considerably speaks rather for the view that the Ag^+ ions are the main active components. Should this suggestion prove, on further investigation, to be well founded, an interesting explanation of the great reactivity of bromo-fatty acids with silver salts may be given on the basis of considerations developed in a previous paper (compare *Trans.*, 1909, **95**, 1839). It has been suggested that the relatively slow reaction between $\text{CH}_3\text{CHBrCOO}'$ ions and OH' ions is connected with the mutual repulsion of the negative charges, and it may therefore be anticipated that the reaction between the $\text{CH}_3\text{CHBrCOO}'$ ion and a positively charged ion (in this case the Ag^+ ion) will be relatively rapid (compare table, *loc. cit.*, p. 1835).

The interpretation of the results is complicated by the equilibria represented by equations (1), (2), and (3) (p. 361). An attempt will be made to prepare pure silver bromopropionate and measure its reactivity, but owing to the great instability of the salt it will probably be difficult to obtain trustworthy results.

In conclusion, I desire to thank Mr. R. W. Davies and Mr. T. J. Ward, of St. Mary's Hospital Medical School, for valuable assistance in the experimental part of the work.

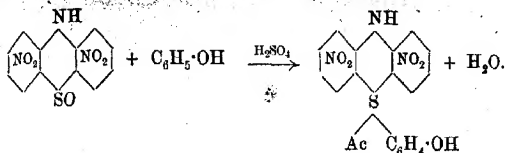
CHEMICAL DEPARTMENT,
ST. MARY'S HOSPITAL MEDICAL SCHOOL, W.

XI.—Derivatives of S-Phenylphenazothionium. Part III.

By EDWARD DE BARRY BARNETT and SAMUEL SMILES.

In two previous communications (Hilditch and Smiles, *Trans.*, 1908, **93**, 145, 1687) the products obtained by the condensation of the nitrodiphenylamine sulphoxides with phenol and phenetole were described. Reasons were then adduced for regarding these sub-

stances as derivatives of *o*-phenylphenazothionium, the process by which they are formed being formulated as follows:

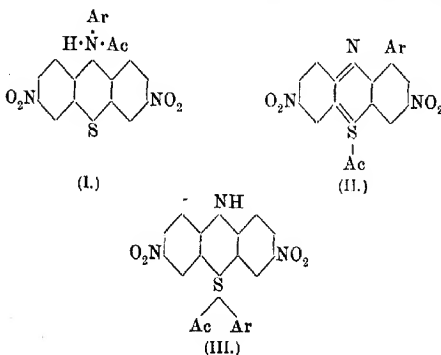


In the meantime the study of the intramolecular rearrangement of the diphenylamine *o*-sulphoxides (Trans., 1909, **95**, 1253; this vol., p. 186) has enabled us to obtain evidence throwing further light on the formation and reactions of these substances. We have therefore extended our experiments with derivatives of this group in order further to discuss their constitution and chemical behaviour.

In the first part of this paper the constitution of these derivatives is discussed, and in the latter part the factors governing their formation are considered.

I.—The Constitution of the Derivatives.

When dinitrodiphenylamine *o*-sulphoxide is treated with a phenol or its ether in presence of concentrated sulphuric acid, the sulphates of the dinitro-compounds of the group are formed. In discussing the constitution of these substances, it has been pointed out (Trans., 1908, **93**, 1688) that on general grounds only three alternative structures can be entertained; these respectively involve the *N*-aryl (I), the *C*-aryl (II), and the *S*-aryl (III) arrangements:



Ample reasons have been readily given for rejecting the former alternatives (I and II) and for accepting the *N*-aryl structure as the true representation of these salts. Later experiments have served still further to strengthen this conclusion.

The N-Aryl Structure.—In order further to test the validity of this structure, we have prepared *N*-phenylthiodiphenylamine by means of the reaction devised by I. Goldberg (*Ber.*, 1907, 40, 4525) for the phenylation of aromatic amines, and we find that the properties of this substance and its nitro-derivatives are entirely different from those of the compounds the structure of which is in question.

N-Phenylthiodiphenylamine.

A mixture of 10 grams of iodobenzene, 5 grams of thiodiphenylamine, 4 grams of potassium carbonate, and 0.5 gram of copper iodide was boiled with excess of bromobenzene for eighteen hours in a flask provided with a reflux arrangement. Water was then added, and the volatile benzene derivatives were removed with the aid of a current of steam. The solid residue was boiled with alcohol, and the solution was separated from the residue by filtration. The product remaining in the filtrates usually contains a considerable quantity of unchanged thiodiphenylamine, but by crystallisation of the more soluble portion, *N*-phenylthiodiphenylamine was obtained in short, yellow prisms, which melted at 89–90°:

0.2006 gave 0.5790 CO₂ and 0.0906 H₂O. C=78.7; H=5.0.

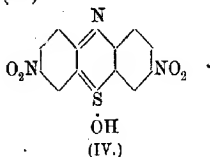
C₁₅H₁₃NS requires C=78.5; H=4.7 per cent.

In chemical behaviour the substance closely resembles *N*-methylthiodiphenylamine. It is soluble in concentrated sulphuric acid, giving a crimson solution, being then partly oxidised to the phenazothionium salt. The basic properties, if, indeed, any are manifest, are very weak, since no salts could be isolated. When nitrated under the conditions required to obtain the dinitro-sulphoxide from *N*-methylthiodiphenylamine, the substance furnishes a mixture of polynitro-compounds, which could not be satisfactorily separated. However, it is sufficient for the present purpose to record the properties of the nitrated substance. It is crystalline, yellow in colour, insoluble in and unattacked by aqueous alkali hydroxide, and, like the corresponding *N*-methyl derivative, may be condensed with phenetole in presence of concentrated sulphuric acid. It is very soluble in cold glacial acetic acid. The following table is given in order to emphasise the distinction between these derivatives and the condensation product obtained from dinitro-diphenylamine *o*-sulphoxide and phenetole:

	<i>N</i> -phenylthio- diphenylamine derivatives	Nitro- diphenylamine derivatives	Condensation product of phenetole and dinitro- diphenylamine sulphoxide.
Colour of base	Yellow	Yellow	Crimson and fluorescent in solution.
Action of acids on base.	No salts formed		Stable green salts obtained.
Action of H ₂ SO ₄ and phenetole.	—	Condensation	Salt formed, but no further action.

The fact that *N*-phenylthiodiphenylamine and its nitro-derivatives do not form salts, whilst the green salts in question are quite stable, is alone sufficient to show that the latter do not contain the *N*-aryl structure. Moreover, if these salts contain the *N*-aryl structure (I), it is clear that the action of alkali must furnish a dinitro-*N*-phenylthiodiphenylamine, but instead they yield crimson, fluorescent bases (Trans., 1908, 93, 151, 1693), which are entirely different from the nitro-derivatives of *N*-phenylthiodiphenylamine. For these reasons the *N*-aryl structure for these compounds must be finally rejected.

The *C*-Aryl Structure (II).—It was previously shown (Trans., 1908, 93, 1689) that if this structure were correct, the substance must be formed by simultaneous oxidation of the phenol and the phenazothionium salt (IV):

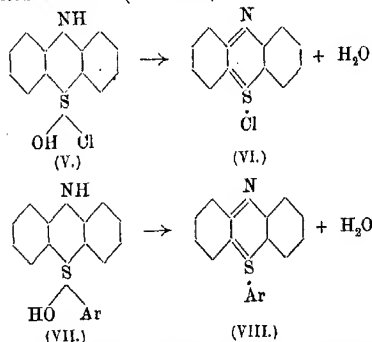


According to this view, the latter substance would appear as an intermediate product formed from the dinitro-sulphoxide (I) by the action of the concentrated acid (see Trans., 1909, 95, 1261). Much evidence has already been adduced for abandoning this view, but, since it is now possible to obtain the dinitrophenazothionium hydroxide in the pure condition, we have been able to submit the question to direct test. Numerous attempts were made to effect the condensation of this phenazothionium hydroxide with phenetole by means of concentrated sulphuric acid both without and in presence of a mild oxidising agent, but they were unsuccessful. In these experiments the greater portion of the phenazothionium hydroxide was unattacked, whilst the remainder was converted into a tarry material from which no definite product could be isolated. However, more cogent argument against this structure is furnished by a comparison of the properties of the dinitrophenazothionium hydroxide and the phenolic compound the constitution of which is sought. It has been elsewhere shown (Trans., 1909, 95, 1256) that

in the former substance (IV) the basic function of the azothionium group is depressed by the presence of the nitro groups in the adjacent benzene nuclei; in fact, the substance does not form salts with aqueous mineral acids. But on examining the formula (II) which represents the *C*-aryl structure for the phenolic compound, it will be seen that, if this were correct, the substance must exhibit a similar lack of basic properties, for it cannot be supposed that these would be strengthened by the linking of a phenolic residue to one of the aromatic nuclei in the azothionium complex. Since all the dinitro-compounds of this group which have been obtained exhibit well-defined basic properties, it is clear that they cannot be derived from the *C*-aryl structure, which for this and other reasons (Trans., 1908, 93, 1689) must now be finally rejected.

The S-Aryl Structure.—This constitution now remains as the only possible alternative, and, as previously shown (Trans., 1908, 93, 1687), it is to be anticipated from the characteristic behaviour of the thionyl group in aromatic sulfoxides, since the latter substances are converted into sulphonium salts by treatment with aromatic compounds in presence of phosphoryl chloride or sulphuric acid. It will now be shown that the *S*-aryl structure is further justified by the analogy between these substances and the parent phenazothionium compounds.

In discussing the mechanism of the change of the imino-thionyl structure into the azothionium arrangement, it has been demonstrated (this vol., p. 186) that in this reaction the thionyl salts are first formed, and that these are subsequently converted into the quinonoid compounds. The process, reduced to its simplest terms, is represented as follows (V and VI):

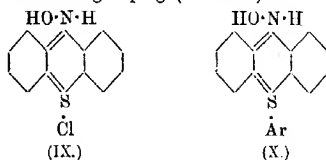


Now, when the *S*-aryl salts are treated with aqueous alkali hydroxide, they are converted by loss of the elements of mineral

acid into ~~crimson, fluorescent bases~~ (Trans., 1908, 93, 145), for which the quinonoid structure (VIII) is accordingly the only representation possible. It is clear that in this process the sulphonium hydroxides (VII) must be first produced by the action of the alkaline reagent, and on referring to the formulae it will be seen that the conversion of these substances into the quinonoid base is strictly analogous to the change of sulphoxide salt into the quinonoid sulphonium salt (V and VI). In either case the quinonoid arrangement is produced by removal of hydroxyl from the quadrivalent sulphur group.

In both series it is possible to obtain the quinonoid derivatives in the hydrated condition. If the green *S*-aryl salts are boiled with water or treated with cold aqueous sodium carbonate, the crimson hydrated bases are formed (Trans., 1908, 93, 151, 1693).

In a previous paper dealing with the salts and hydrates of phenazothionium (this vol., p. 186), we have shown that there is good reason for representing this additional molecule of water as forming the ammonium grouping (as in IX):



If this hypothesis is extended to the *S*-phenyl derivatives, the formula (X) forecasts the possibility of the existence of two series of salts: the green or yellow sulphonium salts (type III), as obtained with the dinitro-derivatives, and a red series, which would be the ammonium salts (type X). We have been able to show that the latter exist. The sulphonium grouping in the dinitro-derivatives which give the green salts is of moderate basic power, and it is evident that if these red ammonium salts exist they must be sought for in derivatives where the basic properties of the sulphonium group are still further depressed. With this object in view the tetranitro-derivative of this series was investigated.

Tetranitro-S-phenetylphenazothionium.

Finely powdered tetranitrodiphenylamine *o*-sulphoxide was mixed with a large excess of concentrated sulphuric acid. Some of the sulphoxide dissolved, but the greater portion remained in suspension. Excess of phenetole was then gradually added to the cold mixture, which was constantly agitated and kept within the limits of atmospheric temperature. As increasing quantities of the

phenolic ether were added to the mixture, the solid dissolved, forming a deep red solution. With further addition of the reagent produced no further change, the mixture was passed through glass wool, and then poured on a large bulk of melting ice. The now insoluble reddish-brown material was collected, well washed with cold water, and finally dried at the atmospheric temperature. This crude material was purified by rapid extraction with acetone in a Soxhlet apparatus. The acetone solution resulting from this operation was concentrated on the water-bath, and then, when cold, it was mixed with a little ether. The first precipitate was removed by filtration and rejected; but on adding a further quantity of ether to the filtrates, *tetranitro-S-phenylphenazothionium sulphate* was gradually precipitated in minute, reddish-brown crystals. Analysis was conducted with two samples from different preparations:

0.1877 gave 0.2728 CO_2 and 0.0553 H_2O . $\text{C}=39.65$; $\text{H}=3.2$.

0.1328 „ 0.1937 CO_2 „ 0.0391 H_2O . $\text{C}=39.8$; $\text{H}=3.2$.

$\text{C}_{20}\text{H}_{13}\text{O}_9\text{N}_5\text{S}_2\text{H}_2\text{SO}_4$ requires $\text{C}=40.2$; $\text{H}=2.5$ per cent.

The substance does not melt below 250° ; it is insoluble in water or cold alcohol, and soluble in acetone. The solutions in the last-named solvent are not fluorescent, like those of the dinitro-compounds.

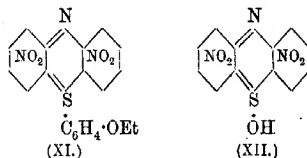
The base is readily obtained in the hydrated form by boiling the sulphate with water. A sample, which had been dried in the steam-oven, was analysed:

0.2014 gave 0.3404 CO_2 and 0.0652 H_2O . $\text{C}=46.1$; $\text{H}=3.6$.

$\text{C}_{20}\text{H}_{13}\text{O}_9\text{N}_5\text{S}_2\text{H}_2\text{O}$ requires $\text{C}=46.4$; $\text{H}=2.9$ per cent.

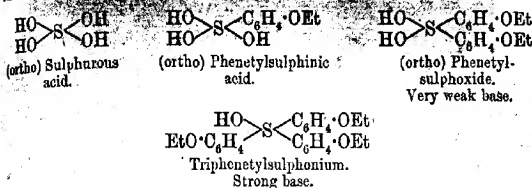
Tetranitro-S-phenylphenazothionium hydroxide is insoluble in water, and very sparingly soluble in boiling alcohol.

Finally, on comparing the dinitro-compounds of the *S*-phenyl series (XI) with those of the parent series (XII):



it is seen that in the former class the basic function of the sulphonium group is appreciably increased by the substitution of aryl for hydroxyl at the quadrivalent sulphur. But it may be remarked that this increase in basic power is to be expected from the general influence of this substitution in simpler compounds of

quadrivalent sulphur. The following series is quoted to illustrate this effect.



and it is clear that the successive replacement of the hydroxyl groups in ortho-sulphurous acid gradually increases the basic power of the group in question.

From these considerations it is seen that the chemical behaviour of the condensation products agrees very closely with that which would be expected for them on the basis of the *S*-aryl structure, from analogy to the simpler phenazothionium hydroxides. Moreover, since all other possible structures have been shown to be untenable, the *S*-aryl constitution must now be regarded as finally established.

II.—Formation of the *S*-Arylphenazothionium Arrangement.

The factors which control the formation of these derivatives are to be found in the nature of the diphenylamine *o*-sulphoxide employed and in the group which is to enter the thionium arrangement. These will be considered separately.

(a) *The Influence of the Character of the Sulphoxide.*—It has been previously mentioned that the derivatives of the *S*-aryl series are obtained by the condensation of a diphenylamine *o*-sulphoxide with an aromatic compound in presence of concentrated sulphuric acid (see formulæ on p. 363). But by no means do all the sulphoxides of diphenylamine behave in this manner. Previous experiments (Trans., 1909, 95, 1253) have shown that, when treated with acid reagents, some of these sulphoxides are immediately converted into salts of phenazothionium (V and VI), and the latter substances are incapable of undergoing the required condensation. It is therefore evident that the answer to the question whether a given sulphoxide can yield the *S*-aryl derivatives by this reaction must depend on the stability of the sulphoxide in presence of the strong acid. If the sulphoxide is instantaneously converted by the acid into the phenazothionium salt, the *S*-aryl derivative will not be formed; but if this conversion does not take place, or if it is sufficiently slow to enable the condensation to be effected before it has proceeded far, then the *S*-aryl derivatives

can be obtained. This is entirely borne out by the behaviour of the six sulfoxides which have been examined:

Sulfoxide.	In concentrated H_2SO_4 .	In concentrated H_2SO_4 with phenetole.
Diphenylamine <i>o</i> -sulfoxide	Immediate rearrangement	No condensation.
<i>N</i> -Methyldiphenylamine "	"	"
<i>pp</i> -Dinitrodiphenylamine "	Rearrangement slow	"Condensation" with fresh solutions.
Diisnitrodiphenylamine "	" "	Condensation with fresh solutions.
Dinitro- <i>N</i> -methyldiphenylamine <i>o</i> -sulfoxide.	" "	Condensation with fresh solutions.
Tetranitrodiphenylamine <i>o</i> -sulph-oxide.	No rearrangement appreciable.	Condensation.

Of these six cases, those of the dinitro-derivatives are the more noteworthy. When phenol is added to freshly prepared solutions of these substances, the *S*-hydroxyphenyl derivatives are readily formed, and the yield is almost quantitative; but with solutions which have been kept some hours, the required reaction does not take place. The intramolecular rearrangement of these sulfoxides which thus militates against the formation of the *S*-aryl derivative is favoured by the increase of the basic function of the thionylphenylamine nucleus (this vol., p. 186). Hence it is clear that the introduction of basic groups in the sulfoxide will tend to hinder the formation of the *S*-aryl compounds, and the addition of acidic groups will tend to exert a favourable influence. This favourable effect seems to attain a maximum in the dinitro-compounds, for these are more reactive and furnish better yields than the tetranitro-derivative. It appears that in these substances the thionyl group is still sufficiently basic to yield readily the sulfoxide salts (V) which form the preliminary stage of the reaction (Smiles and Le Rossignol, *Trans.*, 1906, **89**, 697). The more sluggish condensation of the tetranitro-derivative may be ascribed to the lessened tendency to form these salts, which is due to the further addition of acidic substituents.

(b) *The Nature of the Groups which may enter the Thionium Arrangement.*—Experiments have shown that the chief types of simple aliphatic compounds do not furnish these sulphonium derivatives under the normal conditions of the reaction. The formation of these derivatives seems confined to compounds containing an aromatic complex or an arrangement similar thereto.

The capability of an aromatic compound to condense with the diphenylamine sulfoxide is determined by the reactivity of the aromatic nucleus in the compound in question, and this, in turn, depends on the number and nature of the substituents present.

Of the aromatic hydrocarbons, benzene and toluene are inactive, but if suitable groups are introduced, the condensation can be

readily effected, for example, *m*-xylene acts very sluggishly, but from mesitylene the sulphonium base is easily obtained.

Dinitro-S-mesitylphenazothionium.

Excess of mesitylene was slowly added with constant agitation to a freshly prepared ice-cold solution of *pp*-dinitrodiphenylamine sulphoxide in concentrated sulphuric acid. After each addition of the hydrocarbon, a sample of the liquid was withdrawn and poured into cold water. When the precipitate obtained in this manner was of a pure green colour, the addition of the hydrocarbon was interrupted, and the reaction mixture was poured on powdered ice. The sulphate was then collected and washed, first with water and then with ether, to remove adherent mesitylene and other oily impurities. After renewed washing with water, the salt was triturated with a cold aqueous solution of sodium carbonate. The solid base was collected, and washed with water until free from alkali. After purification, *dinitro-S-mesitylphenazothionium hydroxide* was obtained in minute, chocolate-brown crystals of high melting point. A sample which had been dried at 100° was analysed:

0.2024 gave 0.6660 CO₂ and 0.0868 H₂O. C=59.8; H=4.7.

C₂₁H₁₇O₄N₂S₂H₂O requires C=59.3; H=4.47 per cent.

The base is sparingly soluble in hot water, giving purple solutions, and readily so in cold acetone.

Generally speaking, however, the reactivity of the hydrocarbons is sluggish in comparison with the hydroxy- and amino-derivatives of benzene. Qualitative experiments made with a wide range of material have shown that almost all aromatic compounds containing these groups alone readily furnish the *S*-aryl derivatives with the dinitro-sulphoxides. But since the products obtained from these substances for the greater part resemble the *S*-hydroxy-phenyl and -phenetyl derivatives which have already been described in detail, no particular interest would have been served by the isolation and analysis of each compound. However, the case of the *S*-salicyl derivative is worth especial mention, since it occurs as a true carboxy-thetine.

Dinitro-S-salicylphenazothionium.

The condensation of *pp*-dinitrodiphenylamine sulphoxide with salicylic acid was effected in the usual manner. The crude product, after being well washed with cold water, was dissolved in dilute aqueous alkali hydroxide. The solution was then clarified by filtration, and then mixed with dilute sulphuric acid in exactly

sufficient quantity to precipitate the substance from the solvent could be found for the recrystallisation of this substance. It is soluble in hot nitrobenzene but on cooling the solution it is precipitated in the amorphous condition. Analysis was made with a sample which had been washed with alcohol and dried in the steam-oven:

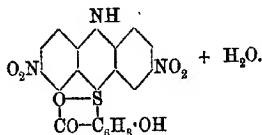
0.2036 gave 0.3858 CO_2 and 0.0608 H_2O . $\text{C}=51.6$; $\text{H}=3.2$.

0.1510 „ 12.5 c.c. N_2 at 23° and 750 mm. $\text{N}=9.4$.

$\text{C}_{12}\text{H}_{10}\text{O}_8\text{N}_2\text{S}$ requires $\text{C}=51.6$; $\text{H}=2.9$; $\text{N}=9.7$ per cent.

Dinitro-*S*-salicylphenazothionium hydroxide forms a mustard yellow, amorphous powder of high melting point.

It is worth observing that the substance obtained in this manner is not the sulphate of the *S*-aryl base which might be expected from analogy to the *S*-hydroxyphenyl derivative. Evidently the sulphonium salt is internally formed with the carboxyl group, the additional molecule of water being present as with most thetines and betaines:



The substance is more stable than the salts of the *S*-hydroxyphenyl series, being unattacked by boiling water; but it is soluble in alkali, giving deep red solutions of a sodium salt.

Turning to the condensation products obtained from naphthalen derivatives, it has been found that the wide scope of the reaction observed with benzenoid compounds is well sustained. Although naphthalene itself does not react with the dinitro-sulphoxides, all hydroxy- and amino-derivatives which have been examined readily form the *S*-naphthyl derivatives. These possess well-defined tinctorial properties, and when sulphonic groups are present the compound is readily soluble in cold water; but the simple hydroxy- and amino-derivatives are sparingly soluble. Some of the chief examples of the *S*-naphthyl derivatives are described in the following table:

Condensation of the *pp*-Dinitro-sulphoxide with

	Colour.
<i>α</i> -Naphthylamine	Purple; sparingly soluble.
<i>β</i> -Naphthylamine	Reddish-brown; sparingly soluble.
<i>α</i> -Naphthol	Blue; sparingly soluble.
2-Naphthylamine-6:8-disulphonic acid ..	Crimson; soluble.
2-Naphthylamine-6-sulphonic acid	Crimson; „
1-Naphthol-6:8-disulphonic	Brown; „ violet in alkali
1-Naphthol-6:8-disulphonic	Crimson; „
1-Naphthol-6-sulphonic	Olive green, violet in alkali.

Attempts to form *S*-aryl derivatives in the crystalline state have been unsuccessful, and they persistently remain in the colloidal condition. The physical properties of the *S*-naphthol derivative are perhaps worth special mention. After undergoing a process of purification, this substance was finally obtained as a blue, viscous jelly, which, on being broken by shock, exhibited a dry fracture.

These *S*-aryl derivatives of phenazothionium are not formed by all aromatic compounds, the most prominent exceptions being the simple nitro-derivatives of benzene and naphthalene. From a general point of view the reaction may be said to be controlled by conditions similar to those observed in the process of sulphonation (Trans., 1908, 93, 745), but hitherto the influence of the so-called steric conditions has not been observed. The resemblance between these processes is not surprising, since the formation of the *S*-aryl phenazothionium salts from the sulphoxides is evidently analogous to the third stage in the ordinary process of sulphonation where the triaryl-sulphonium salt is formed from the sulphoxide.

Finally, it is necessary to point out that the condensation of the thionyl group in the dinitro-sulphoxide is not confined solely to aromatic compounds. For example, thiophen readily furnishes the *S*-thienyl derivative.

S-Thienylphenazothionium.

The condensation of thiophen with *pp*-dinitrodiphenylamine sulphoxide was effected in the usual manner; but since much charring takes place during the reaction, the reagents were employed only in small quantity at each operation, and the temperature was kept below 5°. The impure sulphate, obtained by pouring the united reaction mixtures into water, was collected, washed first with water, and then with alcohol, and finally triturated with aqueous sodium carbonate. The impure base was collected, washed, and dried in the steam-oven. The dry product was crushed to a fine powder, and rapidly extracted with a little acetone to remove soluble impurities. The remaining product was crystallised from boiling phenetole, which, on cooling, deposited *dinitro-S-thienylphenazothionium hydroxide* in large, red prisms, which exhibited a steel-blue lustre. The substance is very sparingly soluble in cold acetone, and does not melt below 250°:

0.2032 gave 0.3828 CO₂ and 0.0330 H₂O. C=50.6; H=1.8.

C₁₆H₉O₄N₂S₂·½H₂O requires C=50.5; H=2.6 per cent.

From the analytical data it appears that the normal sulphonium hydroxide has lost water during the recrystallisation from the high

boiling solvent; unfortunately the quantity of material was too small to enable the analysis to be repeated.

In conclusion, we desire to express our thanks to Dr. Cain for kindly lending us samples of the various amino- and hydroxy-sulphonic acids of naphthalene which were employed in this investigation. We also wish to thank the Research Fund Committee of the Society for a grant which has defrayed the expense of this research.

THE ORGANIC CHEMISTRY LABORATORY,
UNIVERSITY COLLEGE, LONDON.

XLI.—*Apparatus for Demonstrating the Electrolysis of Hydrochloric Acid.*

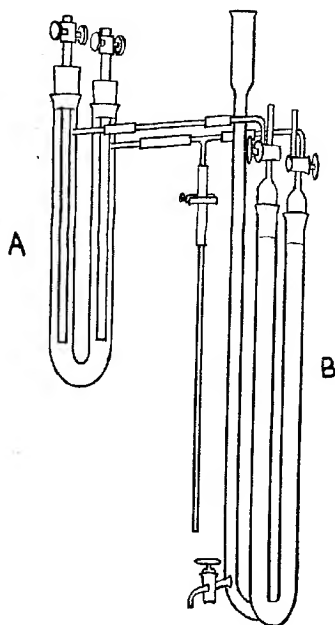
By AUGUSTUS EDWARD DIXON and JOHN TAYLOR.

THOSE who have occasion to use Hofmann's apparatus for showing the electrolytic decomposition of hydrochloric acid into equal volumes of its constituent gases, soon become aware that its comparative simplicity has been attained only at the cost of some disadvantages. Of these it is sufficient to mention (i) the leakage of the acid electrolyte at the bottom of the H-shaped tube; (ii) a difficulty in ascertaining when the saturation with chlorine is complete; and (iii) the possibility, in certain circumstances, of the two gases becoming mixed. Various devices have been proposed to obviate these troubles; they are, however, not very satisfactory in practice, and in any case, when it comes to the final demonstration, there is always distinct inequality between the volumes of the liberated gases.

In L. Meyer's improved apparatus (*Ber.*, 1894, 27, 850), the simplicity is abandoned; for, whilst Hofmann's original form of voltameter is retained, the gases are delivered apart, under diminished pressure, into separate tubes, one of which, containing water, serves to collect the hydrogen; the other, filled at first with saturated chlorine-water, receives the chlorine; each of these tubes, open below, stands in a trough of the liquid with which it is charged. Over the earlier form Meyer's modification has one distinct advantage, since by means of it the equality in volume of the resultant gases may be demonstrated; on the other hand, not only ~~must~~ saturated chlorine-water be prepared, and the collecting

tube filled with it, but also the exposure, on the lecture-table, of an open dish charged with this liquid is not free from objection. Moreover, the three disadvantageous features mentioned above are not eliminated.

The apparatus here figured, although less simple than that of Hofmann, is sufficiently compact to be set up on a single stand, and in practice has given results that are satisfactory. Briefly, it consists of two parts: A, the electrolyser, and B, the vessel for



receiving and measuring over concentrated sulphuric acid the gases delivered from A.

The electrolyser is a U-tube of 1-inch bore, having near each end a delivery tube, as shown; a well-paraffined cork in each neck carries a half-inch carbon cylinder, one foot long; to the projecting free end of this rod a brass binding screw is clamped.

The collecting and measuring vessel is a tall U-tube, of some five-eighths to three-quarters of an inch in bore and about 14

inches long, to the lower end of the tube (the pressure tube) is sealed as shown, and a glass tube, above the highest point of the U, at the foot of the pressure tube, just where it begins to bend upward, is sealed on a light glass tap, having its axis parallel to the plane of the U-tube. Into the top of each measuring tube is ground a hollow glass stopper, which terminates in an obliquely bored two-way tap, communicating at will, either with a short stand-tube of about one-eighth of an inch in bore and an inch or so in length, or with the bent receiving tube, just alongside; the distance between the latter and its fellow of the opposite side is such that each is in a straight line with the corresponding delivery tube of the electrolyser.

By suitable pieces of glass and rubber tubing, the two main parts are connected as shown, the hydrogen-connexions being made with butt-joints and thick-walled rubber tube, well smeared inside with glycerol; between the chlorine delivery tube and the corresponding receiving tube a T-piece may conveniently be introduced; this, when provided with rubber connexion, pinchcock, and glass delivery tube, serves to pass the waste chlorine, when desired, to the table-draught, or into a beaker of lime.

When the electrolyser is filled, the electrolyte may reach to within an inch of the delivery tubes. The receiver is charged in all three limbs to the level of the bottoms of the stoppers, where ground in to the measuring tubes; the sulphuric acid used for filling may be stained, if the operator wishes, by a method given below. The parts are now connected; the pinchcock is opened, both gas-taps are turned into position for receiving, and the plug of the one for hydrogen pulled out sufficiently to allow this gas when liberated, to pass freely out from the electrolyser into the

The current is now turned on, and maintained until the chlorine is seen to be escaping freely. To ascertain if saturation is complete, the pinchcock is closed, the chlorine-tap pulled out for a moment from its seat to equalise pressure, then both taps are pushed home simultaneously, and the lowest tap is turned on, so that the gases may accumulate in the collecting tubes under a pressure not greater than the atmospheric, or less, as may be desired. There is no difficulty in knowing if saturation is complete, for, when this stage is attained, the two tubes fill at exactly the same rate from start to finish.

To recharge the collecting vessel, the pinchcock is opened, the plug of the hydrogen-tap pulled out as at first, and the sulphuric acid, which was drawn off, is returned to the apparatus through the bulb at the top; after this the procedure is as before. When

the products of the reaction in small volumes has been demonstrated, and may be returned to the bulb, and the gases displaced through the two short stand-tubes, may be proved, in the usual way, to be hydrogen and chlorine respectively.

It is scarcely necessary to mention that the slowness (one can hardly call it speed) of saturation with chlorine varies considerably, according to whether the electrolyte is hydrochloric acid alone, the same saturated with salt, or saturated brine; in every case the odorousness is, of course, much reduced by preliminary saturation of the electrolyte with chlorine.

In conclusion, a few points may be noted. The gas-taps should be smeared with vaseline as lightly as will suffice to render them gas-tight; otherwise more or less chokage may occur; the butt-joints, etc., are recommended for the hydrogen connecting tubes on account of the facility with which this gas escapes through rubber; and the cork joints, of course, must be made tight with paraffin or other suitable luting; also, the carbon rods, when done with, should be well washed and dried, to prevent disintegration. It is not easy for persons sitting at a distance to see clearly the accumulation in a narrow tube of colourless or faintly-coloured gases over a colourless liquid. With the apparatus here described, this difficulty may be overcome by dissolving in the sulphuric acid enough chrome-alum to stain it deep green; if between the collecting tubes and the pressure-tube a sheet of milk-glass be interposed, with a light close behind, the filling of the former is rendered easily visible from any part of an ordinary lecture-room. The glass parts of this apparatus were made by Messrs. Baird and Tatlock, in accordance with drawings supplied to them.

UNIVERSITY COLLEGE,
CORK.

XLII.—*The Solubility of Potassium Sulphate in Concentrated Aqueous Solutions of Non-Electrolytes.*

By JOHN JACOB FOX and ARTHUR JOSIAH HOFFMEISTER GAUGE.

IN a recent communication (Trans., 1909, 95, 885) one of us showed that the solubility of potassium sulphate in water at 25° was decreased markedly by the presence of potassium acetate. Since the rate of the decrease is much greater with the more dilute solutions of potassium acetate, which are dissociated electrolytically to a greater degree than the stronger solutions, the

presence of the potassium due to ionised potassium acetate might be considered as being the main factor in decreasing the solubility of potassium sulphate as distinct from the general effect of the second substance in solution, in this case non-ionised potassium acetate. With the view of gaining some further knowledge as to the action as precipitant of the second substance in solution, it was thought desirable to determine the effect on the solubility of potassium sulphate of a number of non-electrolytes, and to ascertain whether the nature of the non-electrolyte was to any marked degree concerned in the action. In the case of potassium sulphate a few determinations of this character have already been carried out, and the general result, both with electrolytes and non-electrolytes, is that the solubility of potassium sulphate in aqueous solution is depressed. From the point of view of the present communication the results of most interest are those of Girard (*Bull. Soc. chim.*, 1885, [ii], 43, 552) for the solubility of potassium sulphate in aqueous ammonia, and of Rothmund and Wilsmore (*Zeitsch. physikal. Chem.*, 1902, 40, 619) for the solubility in aqueous acetic acid and aqueous phenol.

While these results are similar to those described below, a strict comparison cannot be made, since the alteration of solubility by volume has been used by these observers, whereas we prefer the alteration in solubility referred to a fixed quantity of water. A fair approximation to the depression of solubility by volume can, however, be deduced if it is assumed that the total of the volumes of the potassium sulphate and of the liquid in which it is dissolved does not alter. This gives a volume too great by rather more than 1 per cent. in the stronger solutions of potassium sulphate, and practically correct in the weaker solutions. Thus it was found that aqueous alcohol, D_{25}^{25} 0.9913, yielded a solution containing 7 per cent. of potassium sulphate, and having a density of 1.0499. The density of finely powdered potassium sulphate was found to be 2.656 at 20°/20°. Hence 100 c.c. of the saturated solution should, from the composition, occupy 101.3 c.c. Similarly, a solution of glycerol and water, containing 7.2 per cent. of potassium sulphate, possessed a density of 1.1029, the original glycerol and water having a density of 1.0420. The calculated volume of 100 c.c. is 101.2 c.c. As most of the solutions contain less than 7 per cent. of potassium sulphate, the errors introduced are less. Using these calculated volumes, it will be found that the nature of the curves obtained is similar to that of Rothmund and Wilsmore referred to above.

The substances used by us were ethyl alcohol, ethylene glycol, glycerol, mannitol, chloral hydrate, sucrose, acetone, and pyridine.

The solutions were examined partly from the point of view of the possible formation of definite hydrates, since it was thought possible that if with any mixture a simple hydrate was formed, a change in the solubility curve at this point would be found. With this object, mixtures with water in all proportions were taken, and the solubilities plotted against the percentage composition of the aqueous solution.

This method of plotting was chosen in preference to the method of reference to a fixed quantity of water, because of the difficulty of deciding whether water should be considered as solvent or solute in concentrated solutions.*

It is obvious from the curves that as the number of hydroxyl groups in the molecule increases, the precipitating effect of the non-electrolyte decreases, and if the curves are drawn with molecules of potassium sulphate as ordinate and non-electrolyte as abscissæ, taking 1000 molecules of water as fixed, the result is the same. Whether this would be found to apply to other salts cannot, of course, be decided without further investigation. None of the curves give any indication of discontinuity, so that on this view the existence of definite simple hydrates is negatived. This does not, of course, imply that the substances dissolved do not form complexes with more or less water, but the most the results set forth here can be said to indicate is that the non-electrolyte and water exert a material influence on each other, the action preventing the water from dissolving the full amount of salt. There is one consideration, however, which is in a measure opposed to the results obtained by Jones and Getman from observations of the depression of the freezing point of aqueous solutions of non-electrolytes (*Amer. Chem. J.*, 1904, 32, 308). From these observations, Jones and Getman conclude that the deviations of the observed values of the freezing point from the theoretical value are due to the formation of complexes of the solute and water; that in so far as some of the water is used up to form hydrates, less water remains to function as solvent for the hydrate, and that therefore abnormally high results for depression of freezing point are obtained. It should follow that if some of the water is prevented from acting as solvent in the case of hydrates, the same effect should be shown when a second substance (for example,

* During the course of this work, a paper by Rothmund appeared (*Zeitsch. physikal. Chem.*, 1909, 69, 523), dealing with a somewhat similar problem, but using comparatively dilute solutions of the various alcohols and other organic substances. Their effects as precipitants were studied in the case of lithium carbonate and other sparingly soluble salts. Rothmund used fixed volume, and this is justified since the volume of the original solutions could be altered but slightly by the dissolution of sparingly soluble salts.

potassium sulphate) is dissolved in water. Philip has demonstrated this to be the case when it is dissolved in aqueous sucrose solutions (*Trans.*, 1907, 91, 711). Now, according to Jones and Getman, alcohol, chloral hydrate, and mannitol do not show any marked tendency to form hydrates, whereas sucrose, and particularly glycerol, show considerable hydration. We should therefore expect alcohol, chloral hydrate, and mannitol to exert less influence on the solubility of potassium sulphate than either glycerol or sucrose. As will be seen from the results here given, the reverse is the case, both alcohol and chloral hydrate being much more marked in their action than glycerol or sucrose, whether the curves are drawn up on the percentage basis as in the figure, or on the basis of a fixed 1000 molecules of water. It may be argued that the results are in part explicable on the assumption that unless ions are hydrated they cannot exist in aqueous solutions, and consequently that the potassium sulphate will not dissolve if the ions derived from it are subjected to conditions which tend to dehydrate them. The presence in solution of hydrated non-electrolytes might be supposed to act in the direction of preventing the ions from obtaining the requisite quantity of water. In such circumstances the ions could only obtain sufficient water at the expense of the hydrate of the non-electrolyte, and the final result would depend on whether ion or non-electrolyte was most effective in obtaining water (see Lowry, *Trans. Faraday Soc.*, 1905, 1, 197). It would also follow that with the increasing concentration of the non-electrolyte the proportion of hydrated non-electrolyte formed would increase, with a corresponding decrease in the hydrated ions. Such an explanation is, however, merely surmise, and does not altogether apply to the strongest non-electrolyte solutions where the water is insufficient to form any hydrate.

EXPERIMENTAL.

The solutions used were made up by weighing both the substance and the water in which it was dissolved. Saturation was obtained by cooling the saturated solution in contact with solid from a somewhat higher temperature to 25° in a thermostat, and by shaking at 25°. The amount of potassium sulphate was determined by direct weighing of the salt after evaporation and ignition, or by estimating the amount of sulphate by means of barium chloride.

The percentage composition of the solutions and the number of molecules of solutes per 1000 molecules of water from which the curves are drawn are as follows:

			Molecules per 1000 molecules of water.	
Alcohol.	Potassium sulphate.	Water.	Alcohol.	Potassium sulphate.
1.35	9.17	89.48	5.9	10.6
4.80	6.90	88.30	21.3	8.1
7.80	4.96	87.24	35.0	5.9
9.70	4.32	85.98	44.2	5.2
12.34	3.57	84.09	57.4	4.4
14.51	2.71	82.78	68.6	3.4
15.26	2.66	82.08	72.7	3.3
20.50	1.83	77.67	103.2	2.4
26.91	0.97	72.12	146.1	1.4
35.97	0.41	68.62	—	—
43.90	0.22	55.88	—	—
69.26	0.016	30.72	—	—

Aqueous Pyridine—Potassium Sulphate.

			Molecules per 1000 molecules of water.	
Pyridine.	Potassium sulphate.	Water.	Pyridine.	Potassium sulphate.
4.23	7.95	87.82	11.0	9.4
13.90	4.77	81.33	38.9	6.1
24.51	2.75	72.74	76.8	3.9
34.19	1.47	64.34	121.1	2.4
46.29	0.45	53.26	198.0	0.9
55.93	0.12	43.95	—	—
75.90	0.006	24.09	—	—

Aqueous Ethylene Glycol—Potassium Sulphate.

			Molecules per 1000 molecules of water.	
Ethylene glycol.	Potassium sulphate.	Water.	Ethylene glycol.	Potassium sulphate.
3.16	9.67	87.17	10.5	11.5
9.78	7.69	82.53	34.4	9.6
18.47	5.74	75.79	70.8	7.8
32.11	3.57	64.32	145.0	5.7
49.03	1.83	49.14	289.7	3.8

Aqueous Chloral Hydrate—Potassium Sulphate.

Chloral hydrate.	Potassium sulphate.	Water.	Molecules per 1000 molecules of water.	
			Chloral hydrate.	Potassium sulphate.
6.44	9.13	84.43	8.3	11.2
9.09	8.41	82.50	12.0	10.5
12.38	7.79	79.83	16.9	10.1
13.20	7.31	79.49	18.1	9.5
22.07	5.88	72.05	33.4	8.4
33.15	4.54	62.31	58.0	7.5
44.40	3.36	52.24	92.6	6.6
47.30	2.92	49.78	103.5	6.1
62.82	2.00	35.18	194.5	5.9
70.28	1.75	27.97	273.8	6.5
80.26	1.40	18.24	—	—
85.26	1.08	13.66	—	—

Aqueous Glycerol—Potassium Sulphate.

Glycerol.	Potassium sulphate.	Water.	Molecules per 1000 molecules of water.	
			Glycerol.	Potassium sulphate.
8.96	8.37	82.17	21.3	11.2
13.36	7.69	78.95	33.1	10.1
20.34	6.47	73.19	54.4	9.1
24.15	5.38	70.02	67.5	8.6
33.73	4.44	61.83	106.8	7.4
40.40	3.65	55.95	141.4	6.7
43.52	3.33	53.10	160.4	6.6
50.18	2.69	47.13	208.4	5.9
57.22	2.07	40.71	275.1	5.3
67.94	1.53	30.53	—	—
73.18	0.98	20.84	—	—
98.28	0.73	0.99	—	—

Aqueous Mannitol—Potassium Sulphate.

Mannitol.	Potassium sulphate.	Water.	Molecules per 1000 molecules of water.	
			Mannitol.	Potassium sulphate.
3.20	10.32	86.48	3.7	12.3
5.82	10.07	84.11	6.3	12.3
3.35	9.61	82.04	10.1	12.1
11.26	9.19	79.55	14.0	11.9
14.30	8.66	77.04	18.4	11.6
17.22	8.35	74.43	22.9	11.6

Aqueous Sucrose—Potassium Sulphate.

Sucrose.	Potassium sulphate.	Water.	Molecules per 1000 molecules of water.	
			Sucrose.	Potassium sulphate.
9.56	9.85	80.79	6.2	12.3
18.55	8.65	72.80	13.4	12.3
28.16	7.42	64.42	23.0	11.9
37.24	6.35	56.41	34.8	11.6
47.55	5.21	47.24	52.9	11.4
57.00	4.24	38.76	77.5	11.3

Aqueous Acetone—Potassium Sulphate.

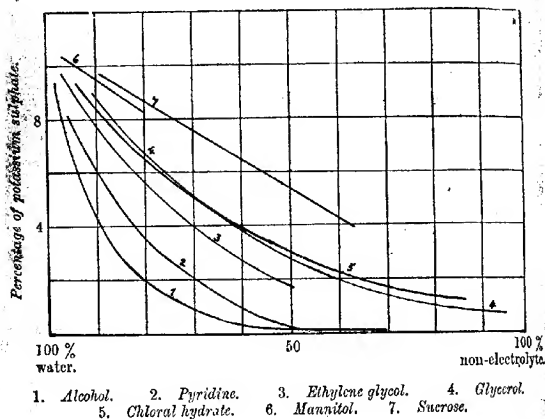
Acetone.	Potassium sulphate.	Water.	Molecules per 1000 molecules of water.	
			Acetone.	Potassium sulphate.
4.92	7.20	87.88	17.4	8.5
10.06	5.02	84.92	36.7	6.1
16.23	2.96	80.81	62.3	3.8
24.31	1.50	74.19	101.7	2.1
37.19	0.47	62.84	185.2	0.8
46.29	0.20	53.51	268.5	0.4
62.40	0.03	37.57	—	—

Certain of the curves (p. 384) require some consideration. Pyridine dissolved in water affords some evidence of the formation of a hydroxide from the fact that it precipitates ferric hydroxide from aqueous solutions of iron salts. When drawn up on the basis of a fixed amount of water, this curve cuts the alcohol curve. It was observed that above the temperature of 45° two liquid phases formed at all concentrations above 5 per cent. and below 46 per cent. approximately. The position of the chloral hydrate curve close to the glycerol curve appears to us to demonstrate that the cause of the depression of solubility is similar in both cases, which does not support the deductions of Jones and Getman (*loc. cit.*) as to the remarkable difference in hydration of these two substances. It will be seen that if the chloral hydrate curve is expressed molecularly with reference to 1000 molecules of water, the end of the curve begins to rise slightly, suggesting that potassium sulphate is soluble in absolute chloral hydrate. An actual determination with liquefied chloral hydrate at 45° gave the solubility as 0.38 per cent. of potassium sulphate.

Glycerol of 99.0 per cent. strength dissolved 0.73 per cent. of potassium sulphate, an amount which is much greater than would be dissolved by the water present. It must be concluded that glycerol also dissolves potassium sulphate.

Both the mannitol and the glycerol curves are straight lines. In other words, the degree of the solubility of potassium sulphate in concentrated solutions of these two substances varies directly as the amount of solute present originally, so that the decrease, if due at all to hydration of the solute, requires the same degree of hydration at all concentrations. This is inadmissible on the usual assumption that the degree of hydration depends upon the amount of water. The mannitol curve could not be carried further than the point shown, which is very close to the saturation point of mannitol.

The solubility in aqueous acetone of varying concentrations expressed per 1000 molecules of water gave a curve which followed



the alcohol curve closely, but fell somewhat below it. Acetone was therefore found to possess the greatest precipitating effect of the non-electrolytes examined.

Both pyridine and absolute alcohol dissolve minute quantities of potassium sulphate, but the amount was too small for accurate estimation. Schiff (*Annalen*, 1861, 118, 362) determined the solubility of potassium sulphate in aqueous alcohol at 15°, and gave four points only. This curve, as far as it goes, runs parallel with and a little below the one given here.

It is of interest to compare the curve for solubility in potassium acetate solutions with the foregoing curves. The position occupied is well below the alcohol curve, a result which may be accounted for if to the main action of non-ionised potassium acetate is

precipitation of the excess of the reagents from the solution.

Hydration of the ions of the salt might be considered as a contributory cause of the depression of solubility. As the rate of decrease is for most of the curves greatest with the dilute solutions, this assumption appears to receive some support; but it cannot be considered quite satisfactory as an explanation, if it is borne in mind that the decrease is continuous even in the strong solutions where there is not sufficient water to form hydrates. Dilute solutions are, however, the limiting cases, and here again we find, as usual, that the rules deduced from the dilute do not apply to concentrated solutions. It is hoped that the results of an investigation now proceeding as to the influence of one non-electrolyte on the solubility of another may throw some light on the possibility of the hydration of ions being a contributory cause of the depression of the solubility of salts by non-electrolytes.

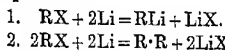
EAST LONDON COLLEGE,
UNIVERSITY OF LONDON.

XLIII.—*The Action of Calcium and Lithium on Organic Halides.*

By JAMES FREDERICK SPENCER and GWYNEDD MARY PRICE.

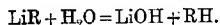
In a previous paper (Spencer and Wallace, *Trans.*, 1908, **93**, 1827) mention was made of a preliminary experiment in which lithium reacted with α -bromonaphthalene with the formation of naphthalene. The present communication describes a series of experiments in which the action of calcium and lithium on organic halogen derivatives has been studied. Lithium reacts with a large number of organic halogen derivatives when the two substances are heated together. In many cases this reaction takes place at the boiling point of the organic compound, but with some substances, notably methyl iodide and bromobenzene, higher temperatures are required, which necessitate the use of sealed tubes. With isopropyl iodide and methyl *p*-bromobenzoate, no reaction took place.

The reaction may be regarded as proceeding in the two directions indicated by the equations:



The products obtained in some cases showed that the reaction had proceeded according to equation 1, for example, those obtained

from *p*-bromotoluene, *p*-chlorophenol, *p*-chloroaniline, and *p*-bromoacetanilide, whilst in other cases the products indicated that the reaction had taken place in both directions. None of the reactions investigated proceeded along the direction indicated by the second equation alone. In all cases white, deliquescent compounds were formed, which reacted with water with the evolution of heat and the formation of the parent substance of the halogen derivative employed. The reaction with water can be represented by the equation:



The white, deliquescent compounds obtained, on the basis of the above equations, consist of mixtures of lithium halide and the lithium derivative of the hydrocarbon. It has been found practically impossible to separate these two substances owing to the ease with which the lithio-hydrocarbon is decomposed by solvents and the atmospheric moisture, but an analysis was made of the whole solid product in the case of the reaction between propyl iodide and lithium, and the results point to the presence of lithio-propane.

The yield of the product in these reactions varies considerably, from about 80 per cent. of the theoretical in the case of *m*-chloroaniline to about 8 per cent. in the case of octyl iodide, but generally they are good.

The reaction products, in all experiments where aniline derivatives were employed, had a strong odour of carbylamine, but this substance was not present in quantity large enough to be isolated. The reaction products in the case of *p*-bromoacetanilide contained much aniline, which is attributed to the hydrolysis of the original product, acetanilide, by the lithium hydroxide during the steam distillation.

The reaction between iodobenzene and lithium was also tried in absolute ether solution under the usual Grignard conditions. No compound other than diphenyl and lithium iodide could be isolated from the reaction products, so that it may be taken that lithium and halogen derivatives in ether solution react according to the Wurtz reaction and not according to the Grignard reaction.

Calcium did not react very readily with organic halides, and in those cases where reaction did occur, the products rarely exceeded 40 per cent. of the theoretical amount. The reaction may be regarded as taking place along two lines, analogous to those of the corresponding reactions with lithium and magnesium (Trans., 1908, 93, 69):

1. $\text{Ca} + \text{RX} = \text{R} \cdot \text{CaX}.$
2. $\text{Ca} + 2\text{RX} = \text{CaX}_2 + \text{R} \cdot \text{R}.$

In many cases, although indication of a reaction was given on heating, the two substances at the boiling point of the organic halide, it was necessary to employ higher temperatures and pressure to cause the action to proceed to any large extent, and in all such cases a considerable quantity of gas was evolved on opening the sealed tubes. The gases evolved consisted of hydrogen and both saturated and unsaturated open-chain hydrocarbons. The solid products were generally white, crystalline, deliquescent substances of the formula RCaX , which were coloured brown by the products of the pyrogenic decomposition of the organic halide.

The products from the reactions with aniline derivatives always had a strong odour of carbylamine, but this substance was not present in sufficient quantity to be isolated. The intermediate compounds of the formula RCaX were extremely difficult to isolate, but in the case of *p*-chlorophenol it was found possible to isolate and analyse the derivative, which agreed well with the formula $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CaCl}$.

E. Beckmann (*Ber.*, 1905, **38**, 905) states that ethyl iodide and calcium react very readily in ethereal solution, with the formation of the compound $\text{C}_2\text{H}_5\cdot\text{CaI}\cdot\text{O}(\text{C}_2\text{H}_5)_2$, the whole reaction being complete in a few minutes. We have repeated this reaction and also the reaction with iodobenzene under similar conditions, and have obtained in both cases products of the type $\text{R}\cdot\text{CaI}\cdot\text{O}(\text{C}_2\text{H}_5)_2$, but the reaction took place very slowly, requiring about twenty hours for completion. The addition of a trace of iodine accelerated it somewhat, but even then it was much slower than indicated by Beckmann.

Metallic calcium, even in inorganic reactions, is difficult to manipulate owing to the insolubility of its derivatives, which generally coat the metal, and thereby stop or greatly impede the reaction. This probably, in addition to a possible superficial coating of oxide on the metal employed, may be the reason for the difficulty experienced in these experiments, and may also explain the poor yields obtained.

EXPERIMENTAL.

In the experiments with lithium, the metal was cut into small pieces under ether, then quickly dried with filter paper, and added to the organic halide. Equimolecular quantities of the metal and halide were used in all cases. The reactions with all the substances tried, except bromobenzene and methyl iodide, took place when heated in a quartz flask, fitted with a condenser, at the boiling point of the halide for periods varying from three to twenty hours.

The reaction products were in all cases white, crystalline, deliquescent solids, which decomposed on the addition of water

with the evolution of heat. The products, after treatment with water, were distilled in a current of steam, and the distillate and the residue in the distilling flask investigated. The results, together with the yields of the products, are given in the table below. The reaction between lithium and iodobenzene was also carried out in ethereal solution, and the sole product formed was diphenyl in small quantity.

The reactions between lithium and bromobenzene and methyl iodide only took place when heated in sealed tubes for about six hours at 250°. The tubes were then cooled in liquid air and opened, and the gases evolved on warming collected and analysed. The residue was then treated with water, and in the case of methyl iodide further quantities of gas were evolved with the evolution of heat. In the case of bromobenzene, benzene was formed, and this was distilled over in steam:

Reacting substance.	Experimental conditions.	Products.
Iodobenzene.....	Heated 1 hour at 188°	70 per cent. benzene & diphenyl
Bromobenzene.....	Heated in sealed tube at 150° for 8½ hours	Benzene and diphenyl
<i>p</i> -Bromotoluene	Heated 1½ hours at 184°	24 per cent. toluene
<i>p</i> -Chlorotoluene	Heated 4½ hours at 150°	7 per cent. toluene; <i>p</i> -ditolyl
<i>m</i> -Chloroaniline	Heated ½ hour at 230°	80 per cent. aniline; <i>m</i> -diamino-diphenyl, traces of carb. amine
<i>p</i> -Chloroaniline	Heated 1½ hours at 230°	68 per cent. aniline, traces of carb. amine
<i>p</i> -Bromoacetanilide.....	Heated 2 hours at 210°	40 per cent. aniline, 12 per cent. acetanilide
<i>p</i> -Chlorophenol	Heated several minutes at 217°	14 per cent. phenol
α -Chloronaphthalene ...	Heated 17½ hours at 263°	Naphthalene; α -dinaphthyl
Methyl iodide	Heated in a sealed tube for 4½ hours at 200°	27 per cent. ethane, 33 per cent. methane mixed with 40 per cent. hydrogen
<i>n</i> -Propyl iodide	Heated 1½ hours at 46-5°	<i>n</i> -hexane; <i>n</i> -propane
<i>sec.</i> -Octyl iodide	Heated 20 hours at 220°	9 per cent. octane; 17 per cent. hexadecane, <i>m. p.</i> 30°

The calcium used in these experiments was the rasped variety supplied by Kahlbaum; it was quite bright and metallic-looking in appearance, but occasionally had a slightly bluish tinge, which may have been due to a superficial coating of oxide. The reactions were first tried at the boiling point of the organic substance used, and as in no case did the reaction proceed to a marked extent, they were then carried out in sealed tubes at temperatures varying from 160° to 250°. The substances were mixed in equimolecular quantities. After cooling, the tubes were immersed in liquid air and opened. No gas was evolved on opening, but on warming to

the atmospheric temperature, gas was evolved, which consisted mainly of hydrogen with small quantities of methane, acetylene, and carbon dioxide. This indicates that calcium, like magnesium (Trans., 1908, 93, 1823), has the property of absorbing large quantities of hydrogen at low temperatures. The solid products were then cautiously treated with water, and any gas evolved was collected and analysed. The aqueous mass was then distilled in a current of steam, and the products, indicated in the table below, collected. The crystalline product of the reaction between *p*-chlorophenol was pressed on a porous plate and then washed with small quantities of absolute ether to remove any unchanged chlorophenol, dried, and analysed:

Found, Ca = 23.1.

$\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CaCl}$ requires Ca = 23.7 per cent.

The lower alkyl halides reacted with calcium when heated at 250° in a sealed tube, but the products could not be obtained, owing to the bursting of the tubes. No matter what precautions were taken, the tubes always burst after they had been heated for about one hour, indicating that a violent reaction had suddenly taken place.

The following table gives a brief summary of the reactions carried out and their products:

Reacting substance.	Experimental conditions.	Products.
Iodobenzene	Heated in a sealed tube at 200° for 16 hours	40 per cent. benzene; 2 per cent. diphenyl
<i>p</i> -Chloroaniline.....	Heated in a sealed tube at 155° for 14 hours	81.5 per cent. aniline
<i>p</i> -Chlorophenol.....	Heated in a sealed tube at 160° for 12½ hours	36 per cent. phenol
<i>p</i> -Bromoacetanilide	Heated in a sealed tube at 200° for 15 hours	Small quantities of aniline and acetanilide, with a trace of carbylamine

CHEMICAL LABORATORY,
BRADFORD COLLEGE, W.

XLIV.—*The Influence of Radium Emanation on Equilibrium in a Gaseous System.*

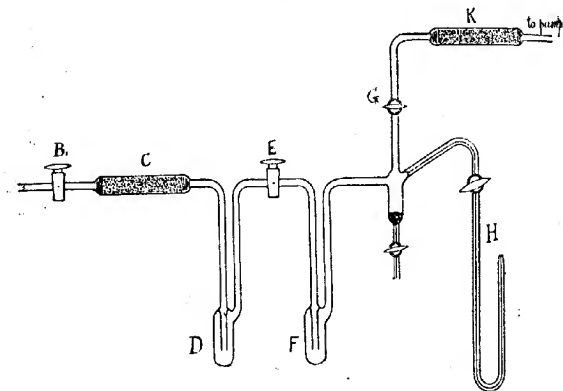
By FRANCIS LAWRY USHER.

SOME interesting deductions concerning the nature of chemical change induced by radium emanation have lately been recorded by Cameron and Ramsay (Trans., 1908, 93, 966) as the result of quantitative experiments on the decomposition of water, ammonia, hydrogen

chloride, and the oxides of carbon, and on the combination of hydrogen and oxygen and nitrogen and hydrogen in presence of the emanation.

The principal conclusions drawn by these authors are (1) that the changes observed are due almost entirely to the α -particles, and (2) that each particle of emanation in disintegrating produces, *ceteris paribus*, the same amount of change. The experiments described are regarded by the authors as preliminary, and the results have qualitative rather than quantitative significance. At the suggestion of Sir William Ramsay, the investigation to be described in this paper was undertaken with the object of obtaining a more definite knowledge of the mechanism of chemical change produced by the emanation,

FIG. 1.



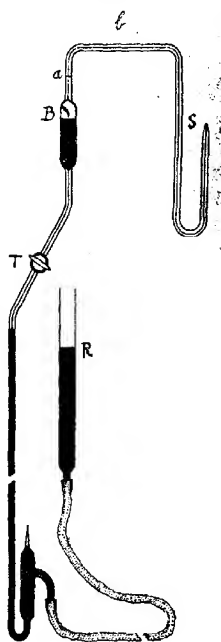
based on an accurate study of the course of some simple reaction. For this purpose, five series of observations have been made, three with pure dry ammonia, and two with a mixture of hydrogen and nitrogen of the composition $3\text{H}_2 + \text{N}_2$.

EXPERIMENTAL.

It will be convenient to describe in detail the method of procedure in the two cases. Fig. 1 represents the apparatus used for the experiments with ammonia. In the first place the tap *B* was closed, and the whole apparatus exhausted by means of a small mercury pump. Ammonia, prepared from pure ammonium chloride and sodium hydroxide, was then introduced through *B* and condensed in the

vessel *D*, which was surrounded with liquid air. *B* was again closed, and the apparatus once more exhausted in order to remove traces of air. The liquid air was removed from *D*, which now contained pure ammonia, and a convenient quantity of this (about 1 c.c.) was pumped off and collected over mercury in a carefully dried gas-tube. *D* was once more cooled with liquid air, so as to condense the ammonia remaining in the apparatus, the tap *E* was closed, and the system on the pump side of *E* thoroughly exhausted. Radium emanation, accumulated during four or five days from a solution containing 0.2111 gram of metallic radium, and mixed with about 0.5 c.c. of hydrogen, was now introduced through the capillary syphon *H*, and *F* was then surrounded with liquid air. After about fifteen minutes, in which time all the emanation had condensed, the hydrogen was removed through the pump, and the required quantity of ammonia, prepared in the way described, was introduced through *H* and frozen in *F* on top of the condensed emanation. If the pump was worked at this stage, traces of gas continued to pass over indefinitely, and an analysis of the gas thus collected showed it to consist solely of hydrogen and nitrogen, so that it appears that solid ammonia is decomposed by the emanation, even at -190° . The drying tubes, *C* and *K*, contained lime freshly prepared from marble. The mixture of ammonia and emanation was next introduced into the apparatus shown in Fig. 2. This consisted essentially of a short length (about 5 cm.) of glass tubing of 1 cm. bore, containing an opaque glass point sealed in so as to form a constant-volume gas chamber, *B*, the volume contained between a mercury surface set to the point and a mark, *a*, on the capillary stem being previously accurately determined by calibration with mercury. The constant-volume chamber was sealed above in a capillary syphon, *S*, and at its lower end terminated above in a capillary syphon, *S*, and at its lower end was sealed to a piece of narrower glass tubing about 80 cms. long, including a stop-cock, *T*, the only one used in the apparatus, which was permanently below the mercury surface and never came into

FIG. 2.



contact with the gas. A mercury reservoir, *R*, of the same diameter as the chamber *B*, was connected with the apparatus by a length of rubber pressure tubing. The greatest care was taken to dry the inner glass surface thoroughly, and for this purpose, before the stop-cock was greased, the entire apparatus was placed in a large air-oven and kept at a high temperature for several hours while a current of dried air was passed through it. In order to introduce the gas, the apparatus was filled with pure dry mercury, and the tube containing the gas was brought over the end of the syphon, *S*, in a mercury trough. By lowering the reservoir, *R*, the gas was admitted, and the end of the mercury thread which followed it was set to the mark *a* on the capillary tubing. The thread was then frozen in the horizontal portion of the capillary at *b* by means of a paper-cup containing solid carbon dioxide, and the tip of the syphon was then sealed with a small blowpipe flame. Finally, the apparatus was fixed up against a glass scale ruled in millimetres, and frequent readings were taken of the pressure exerted by the gas when the mercury surface was set exactly to the point. During the interval between each successive reading, the tap *T* was closed, so that the reaction proceeded at constant volume. It happened, on a few occasions, that after the capillary tip had been sealed and the mercury thread had thawed, the latter was no longer set exactly to the mark *a*, and in such cases the distance between the two was measured and a correction on the volume was made, as the capillary had previously been calibrated by weighing out mercury. In making a reading the temperature of the gas and of the mercury column was carefully noted, and the barometric height was read at the same time.

The above description refers to the experiments with ammonia, but those with nitrogen and hydrogen were carried out in exactly the same manner. The gases were obtained by sparking pure ammonia over mercury in a glass tube. The undecomposed ammonia was removed with a few drops of phosphoric acid, the residual mixture of nitrogen and hydrogen was carefully dried, and a convenient quantity was collected in a tube in the same way as the ammonia, the calcium oxide, however, being replaced by phosphoric oxide. The subsequent procedure differed slightly from that employed in the experiments with ammonia. The apparatus shown in Fig. 1 was modified to some extent, but it will suffice here to say that, after thorough exhaustion of the apparatus through the mercury pump, the previously dried emanation, accompanied by its excess hydrogen, was taken in through a capillary syphon, the emanation was frozen with liquid air, and the hydrogen removed through the pump. Finally, the liquid air was removed, and the sample of nitrogen and hydrogen collected for the experiment was admitted and allowed to mix with

the emanation, the mixture being then pumped off and transferred to one of the reaction vessels already described.

It will be obvious that throughout the whole of the operations just described there is no possibility of serious contamination. It is true that during the process of purification, gaseous emanation was brought into contact with the stop-cocks *H*, *G*, and *E* (Fig. 1), but the total time of contact between tap grease and emanation was certainly less than thirty minutes, and it was proved by a blank experiment with emanation and some of the same rubber tap grease that if oxygen is excluded, the only gaseous product of the action is pure hydrogen, the amount of which produced in half an hour would be quite negligible.

Each experiment was allowed to proceed for at least four weeks, at the end of which period the amount of emanation still present was insignificant. During the first two days, readings were taken every few hours, and afterwards at the rate of about one every twenty-four hours.

At the conclusion of each experiment, the gas was removed from the reaction vessel and analysed, the ammonia, nitrogen and hydrogen, and gases absorbable by potassium hydroxide being determined. Reference will be made to those analyses in the discussion of the results.

Experiment I.—Volume of reaction chamber: 2.1187 c.c. Initial volume of ammonia at 0° and 760 mm. = 0.4514 c.c. About half the quantity of emanation taken for this experiment was accidentally lost, so that the proportion of ammonia to emanation is not known:

Time in days.	Corrected vol. of gas.	Volume increment.	$1/\log V_0/V_c$	$1/E_d \log V_0/V_c$
0.0	0.4514	0.0	—	—
0.56	0.4801	0.029	0.0516	0.0571
0.77	0.4920	0.041	0.0538	0.0620
1.56	0.5183	0.067	0.0448	0.0594
1.83	0.5235	0.072	0.0413	0.0571
2.58	0.5436	0.092	0.0384	0.0615
4.54	0.5765	0.125	0.0301	0.0707
5.54	0.5838	0.132	0.0272	0.074
7.56	0.5956	0.144	0.0221	0.086
9.67	0.6020	0.151	0.0183	0.103
12.58	0.6048	0.153	0.0143	0.137
40.00	0.627	0.176	0.0054	—

Experiment II.—Volume of reaction chamber 8.1655 c.c. Initial volume of ammonia at 0° and 760 mm. = 1.843 c.c. Initial pressure = 474 mm.:

Time in days.	Corrected vol. of gas.	Volume increment.	$1/t \log V_d/V_r$	$1/E_t \log V_d/V_r$
0.0	1.843	0.0	—	—
0.042	1.854	0.011	0.0619	0.0623
0.083	1.871	0.028	0.0801	0.0812
0.104	1.874	0.031	0.0708	0.0720
0.185	1.881	0.038	0.0670	0.0685
0.191	1.891	0.048	0.0601	0.0621
0.865	2.068	0.225	0.0854	0.0764
1.031	2.104	0.261	0.0843	0.0777
1.198	2.145	0.302	0.0849	0.0808
1.854	2.262	0.419	0.0805	0.084
2.042	2.302	0.459	0.0610	0.088
2.185	2.328	0.480	0.0600	0.089
2.840	2.416	0.573	0.0570	0.095
3.230	2.455	0.612	0.0543	0.097
3.840	2.512	0.669	0.0510	0.102
3.958	2.523	0.680	0.0505	0.103
5.840	2.652	0.809	0.0430	0.122
6.896	2.703	0.860	0.0396	0.136
7.840	2.724	0.881	0.0360	0.147
8.840	2.757	0.914	0.0327	0.165
9.840	2.775	0.932	0.0311	0.183
12.886	2.804	0.961	0.0243	0.253
36.000	2.871	1.028	0.0098	—

Experiment III.—Volume of reaction chamber: 2.406 c.c. Initial volume of ammonia at 0° and 760 mm. = 0.909 c.c. Initial pressure = 306 mm.:

Time in days.	Corrected vol. of gas.	Volume increment.	$1/t \log V_d/V_r$	$1/E_t \log V_d/V_r$
0.0	0.909	0.0	—	—
0.031	0.914	0.005	0.0772	0.0776
0.073	0.923	0.014	0.0923	0.0934
0.76	1.037	0.128	0.0848	0.1000
1.08	1.038	0.174	0.0855	0.103
1.75	1.154	0.245	0.0779	0.108
2.08	1.188	0.279	0.0768	0.110
2.78	1.237	0.328	0.0700	0.116
3.75	1.291	0.382	0.0632	0.124
4.75	1.325	0.416	0.0559	0.132
6.75	1.377	0.468	0.0466	0.156
7.76	1.387	0.478	0.0418	0.168
8.75	1.397	0.488	0.0382	0.184
9.75	1.401	0.492	0.0347	0.202
10.76	1.408	0.499	0.0321	0.221
11.76	1.419	0.510	0.0304	0.253
13.77	1.419	0.510	0.0260	0.310
14.76	[1.440]	[0.531]	[0.0258]	[0.359]
15.76	1.419	0.510	0.0227	0.392
32.00	1.433	0.524	0.0117	—

Experiment IV.—Nitrogen and hydrogen. Same tube as in Exp. I.
Initial volume of mixed gases at 0° and 760 mm. = 1.602 c.c. Initial pressure = 615 mm. :

Time in days.	Corrected vol. of gases.	Volume increment.
0.4	1.602	0.0
0.155	1.585	-0.017
0.698	1.540	-0.062
2.698	1.482	-0.140
2.990	1.460	-0.142
3.678	1.442	-0.160
4.010	1.441	-0.161
4.698	1.425	-0.177
11.80	1.403	-0.199
31.89	1.362	-0.240

Experiment V.—Nitrogen and hydrogen. Same tube as in Expt. II.
Initial volume of mixed gases at 0° and 760 mm. = 2.323 c.c. Initial pressure = 594 mm. :

Time in days.	Corrected vol. of gases.	Volume increment.
0.0	2.323	0.0
0.7	2.273	-0.050
1.7	2.247	-0.076
2.7	2.230	-0.093
4.7	2.241	-0.082
5.7	2.228	-0.095
6.7	2.225	-0.098
30.0	2.181	-0.142

The analysis of the gases at the conclusion of each experiment was carried out by means of a small glass burette, provided with a stop-cock and capillary syphon, and containing six opaque glass points. The volume between a mercury surface set to each of these points and a mark on the capillary stem was accurately determined by calibration with mercury, and measurements were made by observing against a glass scale, the difference between the level of the mercury in a reservoir connected with the burette and that of the mercury set exactly to one or other of the points. The measurements are in all cases correct to within 0.002 c.c. The gas was always measured dry, and was, if necessary, for example, after explosion or treatment with a wet reagent, pumped through a small tube of phosphoric oxide. Ammonia was determined by absorption with a few drops of phosphoric acid, hydrogen by explosion with a measured excess of oxygen, and carbon dioxide by absorption with a lump of fused and moistened potassium hydroxide.* The residual gas, after removal of excess oxygen by phosphorus, was measured and considered to be nitrogen. The treatment of the gases with liquid and solid reagents took place in small gas tubes, the gas being completely freed from the reagent

* Any other acid gases, oxides of nitrogen, etc., are consequently called "CO₂."

and dried before introduction into the measuring burette. The following table gives the results of the analyses of the gases at the termination of the experiments:

	I.	II.	III.	IV.	V.
	c.c.	c.c.	c.c.	c.c.	c.c.
NH ₃	0.173	0.78	0.312	0.006	0.010
H ₂	0.927	1.56	0.314	0.980	1.321
N ₂	0.121	0.56	0.298	0.356	0.669
CO ₂	0.002	0.014	0.000	0.019	0.185
CO	0.004	0.004	0.009	0.001	0.003

Discussion of Results.

It is interesting to compare these results with the figures given by Cameron and Ramsay, and for this purpose it is convenient to calculate the values of the expression: $Q = 100 \frac{V_{\infty} - V_t}{V_{\infty} - V_0}$, and the corresponding logarithms, as is done by these authors. These values are given in the following table for Expts. I and III; the reasons for omitting Expts. II, IV, and V will be given presently.

EXPERIMENT I.

Time in days.	$V_{\infty} - V_t$	$Q = 100 \frac{V_{\infty} - V_t}{V_{\infty} - V_0}$	Log. Q.	Log. Q/100/t = -k.
0.00	0.176	100.0	2.000	—
0.56	0.147	83.6	1.922	1.392
0.77	0.135	76.8	1.885	1.494
1.56	0.109	62.0	1.792	1.334
1.83	0.104	59.1	1.772	1.245
2.53	0.084	47.7	1.679	1.243
4.54	0.051	29.0	1.462	1.185
5.54	0.044	25.0	1.398	1.086
7.56	0.032	18.2	1.260	0.879
9.67	0.025	14.2	1.152	0.877
12.53	0.023	13.1	1.117	0.702

EXPERIMENT III.

Time in days.	$V_{\infty} - V_t$	$Q = 100 \frac{V_{\infty} - V_t}{V_{\infty} - V_0}$	Log. Q.	Log. Q/100/t = -k.
0.00	0.524	100.0	2.000	—
0.76	0.396	75.6	1.878	0.161
1.08	0.350	66.8	1.825	0.162
1.75	0.279	53.3	1.727	0.156
2.08	0.245	46.8	1.670	0.159
2.78	0.198	37.4	1.573	0.154
3.75	0.142	27.1	1.433	0.151
4.75	0.108	20.6	1.314	0.144
6.75	0.056	10.7	1.029	0.144
7.76	0.046	8.3	0.944	0.136
8.75	0.036	6.9	0.839	0.133
9.75	0.032	6.1	0.785	0.125
10.76	0.025	4.8	0.681	0.123
11.76	0.014	2.7	0.431	0.133
13.77	0.014	2.7	0.431	0.114

The figures in the last column of the preceding tables represent the constant in the equation $\frac{V_{\infty} - V_t}{V_{\infty} - V_0} = e^{-kt}$, or, rather, the constant calculated with common instead of Napierian logarithms. It will be noticed that the value of $-k$ diminishes fairly regularly with time, and that the underlying assumption, which would require it to remain really constant, does not, therefore, strictly represent the facts.

The time of half action is in Expt. I, 2.4 days, and in Expt. III, 1.9 days, both considerably less than the half-life period of the emanation, which is 3.86 days (Sackur). It seems, therefore, that the simple hypothesis that each atom of emanation in decaying produces the same amount of change, that, in fact, the effect is at any time proportional to the amount of emanation present, although it may be true under certain conditions, requires some modification to make it agree with the experiments here recorded.

Let us assume that the velocity of reaction at any time, t , is proportional, both to the amount of emanation and of ammonia present at that time. Then $-\frac{dv}{dt} = kE_tV_t = KE_tV_t$. Now, during a very small space of time, E_t is constant, so that the above expression can be integrated by keeping KE_t as the constant, and the resulting expression can be subsequently corrected for the variation of E_t . We get then: $\frac{1}{t} \log \frac{V_0}{V_t} = KE_t$.

For the sake of comparison, we may consider that the velocity of decomposition depends only on the amount of ammonia present, and is not influenced by the decay of the emanation. We should then find that $\frac{1}{t} \log \frac{V_0}{V_t}$ was constant. The reaction has been treated as an irreversible-unimolecular one, since it is obvious from the analysis of the gases at the end of Expts. IV and V that recombination takes place to an almost inappreciable extent. Whereas in Expt. III, 65.7 per cent. of the ammonia put in was decomposed, in Expt. IV, starting with nitrogen and hydrogen, only 0.75 per cent. of the mixture was recombined.

The values of $\frac{1}{t} \log \frac{V_0}{V_t}$ and of $\frac{1}{E_t t} \log \frac{V_0}{V_t}$ have already been tabulated for Expts. I to III on pp. 393, 394, and it is interesting to note that while the constant becomes smaller with time when no correction for the decay of the emanation is applied, it becomes larger when the correction is introduced. Obviously, it is unreasonable to omit the correction for decay of the emanation; nevertheless, when the full correction is put in, the constant changes in the opposite direction, although at the same time a distinct improvement is noticeable. It

is here suggested that a third factor, namely, the efficiency of the emanation, is required in order to explain the increase of the velocity constant with time. Since an α -particle is effective over a range of about 8 cm. in ammonia gas under the pressures employed in these experiments, a large proportion of its energy must be wasted when it is enclosed in a tube of 1 cm. bore, although this waste need not be proportionately greater at one time than another; but one atom of emanation is capable, as will be shown later, of decomposing at least 134,000 molecules of ammonia. It is, therefore, highly probable than when, as in Expt. III, the emanation is present in the proportion of 1 atom to 10,850 molecules of ammonia, the efficiency of an α -particle will be greater, as its chance of colliding with a larger number of molecules increases; in other words, each α -particle will do more work when there is more work to do.

It is possible to make an approximate correction by assuming that the efficiency is proportional to the ratio of the number of emanation molecules to ammonia molecules at any time, although of course this cannot be expected to hold over an extended period.

We may assume that $-\frac{dv}{dt} = KE_t V_t \beta_t$, where β_t is the efficiency.

Then if $\beta_t \propto \frac{V_t}{E_t}$, we get $\frac{1}{V_t} \log \frac{V_0}{V_t} = \text{constant}$. This expression gives a much better value for K over a period of six or seven days, starting at one day from the commencement of the experiment, but it afterwards becomes smaller again, a result which is to be expected for two reasons: first, because the assumed correction is the most drastic possible, and can only be strictly valid over a very short range; and secondly, because as the reaction proceeds, the energy of the emanation is more and more used up in useless work, namely, in imparting increased velocity to the accumulating products of decomposition. We can, therefore, make the further assumption [that the efficiency is proportional, not only to the ratio of the amounts of emanation and ammonia, but also to the actual quantity of ammonia present. In this case, $\beta_t = \frac{V_t}{E_t} V_t$, and the velocity constant becomes $K = \frac{1}{\sqrt{E_t V_t} \cdot t} \log \frac{V_0}{V_t}$. The constants calculated in the two ways suggested are tabulated on p. 399 for Expt. III.

The correction appears to be rather too great in the first case, and, slightly too small in the second, but on the whole both sets of constants are much better than when no correction for change in efficiency is introduced. It would doubtless be possible by suitably compromising between the two methods to obtain a still more constant value of K .

* It is probably not worth while to attempt this, because there are

$$\text{Time in seconds } t = \frac{1}{K} \log \frac{P_0/V_0 - P/V}{P_0/V_0 - P/V_1} \log \frac{P_0/V_0 - P/V_1}{P_0/V_0 - P/V_2}$$

0.073	0.103	0.098
0.76	0.111	0.106
1.08	0.116	0.109
1.75	0.117	0.111
2.08	0.121	0.116
2.78	0.120	0.118
3.75	0.120	0.121
4.75	0.113	0.121
6.75	0.106	0.129
7.76	0.097	0.127
8.75	0.091	0.127
9.75	0.083	0.128
10.76	0.078	0.134
11.76	0.076	0.138

slight complications in all the experiments, and these will now be considered.

It will have been noticed in Expt. IV that if the amount of nitrogen and hydrogen recombined is calculated from the observed change of pressure, there should be 0.240 c.c. of ammonia at the conclusion of the experiment. As a matter of fact, the analysis shows that only 0.006 c.c. was formed. The gases and the apparatus were both very carefully dried, there was no contamination by air, and no possibility of leakage during the course of the experiment; the gas was under considerably reduced pressure the whole time. Clearly, then, nearly a quarter of a c.c. of gas had ceased to exert any pressure. We can make up a balance sheet with respect to the total quantity of hydrogen and nitrogen put in at the commencement, and found at the termination, of two typical experiments: Nos. III and IV, reckoning as hydrogen and nitrogen these gases in combination as well as free. This balance sheet gives the clue to the observed discrepancies.

	Hydrogen put in at commencement.	Nitrogen put in at commencement.	Hydrogen found at end.	Nitrogen found at end.
	c.c.	c.c.	c.c.	c.c.
Expt. III	1.363	0.454	1.282	0.454
„ IV	1.201	0.400	0.989	0.359
Hydrogen lost in Expt. III			0.081 c.c.	
Nitrogen „ „ III			0.000 „	
Hydrogen „ „ IV			0.212 „	
Nitrogen „ „ IV			0.041 „	

In Expt. III a small quantity of nitrogen was probably lost, for the first reading was made as soon as possible after, but not at precisely the same moment as, the emanation was mixed with the ammonia. The initial volume therefore refers to a mixture of ammonia with a trace of its decomposition products, and not to pure ammonia, as is assumed for the purpose of the above calculation.

In Expt. IV we find, as one would expect, that a larger proportion of hydrogen and nitrogen is missing, because the partial pressure of these gases is considerably higher than in the preceding experiment, in which no free hydrogen or nitrogen was introduced initially. Now this missing gas can only have disappeared in three ways: (1) it may have reacted chemically with the glass of which the apparatus was made; (2) it may have been driven into the walls of the vessel and remained there, or (3) it may have gone completely through the glass. The first possibility is very unlikely, because nitrogen was lost as well as hydrogen, and the glass did not present the appearance of having been attacked; only the usual brownish-violet coloration was observed.

In order to settle this question definitely, it was decided to carry out a blank experiment with pure hydrogen and emanation, arranged so that any loss of gas could be observed and measured, and so as to detect any gas which might pass right through the glass. In the meantime, the three reaction chambers employed in the five experiments already described were coarsely powdered, placed in a piece of Jena glass tubing, first exhausted cold by a Töpler pump, and finally heated to redness and again exhausted; nearly 2 c.c. of gas were pumped out of the heated glass, and its composition was as follows. The measured total volume was 1.817 c.c.:

CO ₂	1.416 c.c.
CO	0.240 "
H ₂	0.096 "
N ₂	0.066 "
Total	... 1.818 c.c.

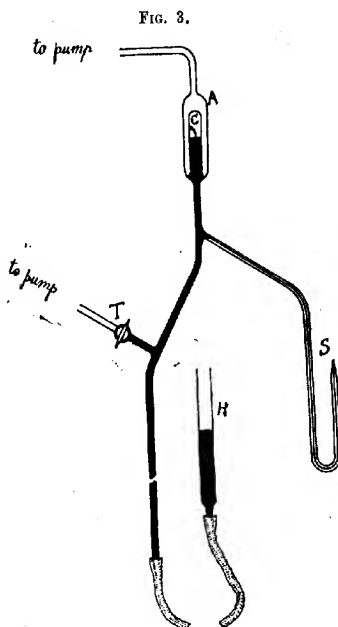
The experiment was rather unsatisfactory, as the powdered glass was not treated with chromic acid to remove traces of grease, dust, etc., before being heated; nevertheless, nearly 0.1 c.c. of hydrogen was recovered, and a rather smaller quantity of nitrogen.

The apparatus used for the blank experiment was made of glass of about the same thickness as that used in the previous experiments. It is diagrammatically sketched in Fig. 3. The constant volume chamber, *C*, containing an opaque glass point, was itself sealed into a wider piece of glass tubing, *A*, which was drawn out at the top and connected, through a small phosphoric oxide tube, with a Töpler pump, no taps being used. The space between the reaction chamber and this outer tube was at the commencement of the experiment very thoroughly evacuated, and the pump with which it was connected was worked from time to time during the experiment in order to collect any gas which might be driven through from the reaction chamber.

The latter was sealed, immediately below the inserted join, to a piece of narrower glass tubing about 80 cms. long, the lower end of which was connected through an air-catch with a length of rubber pressure tubing attached at its distal end to a mercury reservoir, *H*. A small capillary syphon, *S*, was sealed on shortly below the inserted join, and was used for taking in the hydrogen and emanation. Another piece of tubing was sealed on about 4 cms. below the syphon, and was connected through the tap *T* with a second Töpler pump.

Mercury was first poured into the reservoir, and the rubber tubing was clipped when the mercury stood a short distance below the T-piece carrying the tap *T*. The end of the capillary syphon was sealed, and the apparatus was then very thoroughly exhausted through *T*. The latter was then shut, and the reservoir was raised until the mercury stood in the tubing between the lower T-piece and the capillary syphon. The end of the latter was then scratched with a glass knife, and the point was broken off inside a small

gas tube containing the emanation mixed with about half a c.c. of hydrogen, carefully purified and dried. The gas entered the apparatus, and the reservoir was again raised, until the hydrogen and emanation were forced up into the reaction chamber, and the mercury in the reservoir was level with the tip of the capillary syphon; the latter was then sealed in a blow-pipe flame. The entire apparatus was fixed up in front of a glass scale, and frequent readings were taken of the pressure of the gas when the mercury was set to the point. The volume of the reaction chamber was subsequently determined by measuring the pressure of a quantity of dry air introduced into it, and afterwards



removed and re-measured in a constant volume Dumas burette already calibrated.

Throughout this experiment no gas passed through the walls of the reaction chamber into the surrounding vacuous space, which remained quite empty. The amount of hydrogen in the tube decreased, however, from 0.610 c.c. to 0.487 c.c. The following table gives the readings:

Time in days.	Corrected vol. of hydrogen.	Volume decrease.	$K = 1/E_r \log V_0/V_t$
0.00	0.573	—	—
1.15	0.530	0.043	0.0363
1.81	0.514	0.059	0.0355
2.81	0.507	0.066	0.0315
3.81	0.510	0.063	0.0261
4.81	0.505	0.068	0.0270
6.81	0.495	0.078	0.0313
8.81	0.494	0.079	0.0360
15.81	0.490	0.083	0.0711
25.81	0.489	0.084	0.267

The results are not sufficiently regular to admit of their application as quantitative corrections to the experiments with ammonia and with nitrogen and hydrogen. It is even possible that after some time the glass walls of the containing vessel become so pitted by the bombardment that the surface is appreciably altered, and, in any case, the problem is probably much more complicated than it at first appears.

At the conclusion of this last experiment, the reaction chamber was powdered, and the powder was carefully cleared with hot chromic acid, washed, dried, and put in a clean Jena-glass tube and exhausted cold. It was then exhausted at a red heat, and in this way 0.076 c.c. of gas was extracted. Its composition was:

CO ₂	0.014 c.c.
H ₂	0.061 „
Total	0.075 „

There can therefore be no doubt that hydrogen, and, to a smaller extent, nitrogen, is driven into the glass walls of its containing vessel when mixed with radium emanation. The greater part of such gas can be recovered when the glass is strongly heated.

In calculating the velocity constants and the values of the expression Q , it was stated on p. 396 that the reasons for omitting Expts. II, IV, and V would be given later. IV and V were of course omitted because the observed pressure changes do not really indicate recombination of nitrogen and hydrogen, as has just been shown. It will be seen on referring to the analysis of the gas from Expt. II that, although there is an *apparent* loss of

hydrogen, there is more nitrogen at the end than there was at the beginning, and the same is true for Expt. V. There was no ordinary leakage during either of these experiments, but the same apparatus was used for each, and this curious result may be explained on the hypothesis that there were bubbles in the glass vessel at its junction with the capillary tubing at its upper end, and that the glass was so thin in the region of these bubbles as to become perforated by the α -particles, and so allowed a slow diffusion of air from without. Unfortunately, the discrepancy was not discovered until after the tubes had been ground up.

Chemical Efficiency of the Emanation.

It has been pointed out that in all the experiments hitherto described, the emanation probably brings about only a fraction of the amount of decomposition which it could effect under more favourable conditions. In Expt. III the total volume of ammonia decomposed was 0.597 c.c., and the emanation which was mixed with it was the product of six days' accumulation, and therefore, according to the recent work of Gray and Ramsay (*Trans.*, 1909, 93, 1073), 0.000081 c.c. In this experiment, then, the ratio of the volumes of emanation and ammonia was 1 to 7380, or, in other words, each atom of emanation decomposed on the average 7380 molecules of ammonia.

In order to get some idea of the amount of chemical work which could be done by the emanation under favourable conditions, an experiment similar to those described above was carried out on a much larger scale. A large round-bottomed flask of 2 litres capacity was filled with ammonia at about 260 mm. pressure, and mixed with six days' accumulation of emanation. The course of the reaction could not, of course, be followed, but, at the end of a month, the gases were pumped out and the quantity of nitrogen and hydrogen produced was roughly estimated. It was found that 10.9 c.c. of ammonia had been decomposed. This is, in every sense, a minimum value, for no account is taken of the fact that that portion of the emanation which was near the walls of the flask was not entirely used up in decomposing ammonia, and no correction is introduced for gas driven into the glass.

There is, however, no doubt that the conditions of this experiment were extremely favourable as compared with those of the preceding ones, and were probably such as to secure at least 90 per cent. of the maximum amount of decomposition. In this case, one molecule of emanation decomposed 134,300 molecules of ammonia.

If we take this as an approximate measure of the chemical efficiency

of the emanation, we can calculate the fraction of the total energy of the emanation which is used in effecting chemical decomposition.

It is reasonable to assume that the α -particles are mainly responsible for the effects observed, and, further, that their power to decompose ceases when they no longer produce any other physical effect, that is, when their velocity is reduced to 64 per cent. of their average initial velocity of projection.

On this hypothesis, the total kinetic energy of one atom of emanation available for chemical work will be that of three α -particles, since the atoms of radium-A, -B, and -C are projected with less than the critical velocity.

Now, the total kinetic energy of one α -particle is 6×10^{-6} ergs, hence the energy available for chemical work $= (6 \times 10^{-6}) \times (0.64)^2 =$ about 2.5×10^{-6} ergs.

Therefore one atom of emanation produces about 7.5×10^{-6} ergs. available energy. Taking the mechanical equivalent of heat as 4.182×10^7 ergs. per calorie, this amounts to

$$\frac{7.5 \times 10^{-6}}{4.182 \times 10^7} = 1.8 \times 10^{-13} \text{ calories.}$$

Now, 134,300 molecules of ammonia (which are decomposed by one atom of emanation) require for complete decomposition about 2.02×10^{-15} calories, hence the chemical efficiency of the α -particle in this experiment is

$$\frac{2.02 \times 10^{-15}}{1.8 \times 10^{-13}} = 1.12 \times 10^{-2},$$

or a little more than 1 per cent.

As regards its influence on equilibrium in the system ammonia-hydrogen-nitrogen, it can only be said that if any definite state of equilibrium were reached under ideal conditions, it would be one corresponding with a very high temperature. Under ordinary conditions there is no true equilibrium, but only a state of rest depending on the proportions of ammonia and emanation, surface, and possibly other factors as well. The emanation cannot be called a catalyst in any sense, and the effects produced are probably mechanical or electrical in origin.

The principal conclusions arrived at in the course of this investigation may be summarised as follows:

- (1) Ammonia is decomposed by radium emanation at the ordinary temperature, and the decomposition is nearly irreversible.
- (2) Recombination was not observed to take place to a greater extent than 0.86 per cent.
- (3) Decomposition of solidified ammonia by solidified emanation proceeds with appreciable velocity at -190° .

(4) The decomposition at the ordinary temperature follows approximately the course of a unimolecular homogeneous reaction when correcting factors for the decay of the emanation and alteration of its efficiency with time are introduced.

(5) If the ratio of ammonia to emanation molecules does not exceed 10,000 to 1, the statement that each atom in disintegrating produces the same effect is not strictly true, on account of the waste involved when the system is rich in emanation.

(6) The largest effect observed was the decomposition of 134,300 molecules of ammonia per atom of emanation.

(7) The energy required to produce the largest effect observed was about 1 per cent. of the energy actually expended during the production of that effect.

(8) All experiments with gases in glass vessels in presence of the emanation are complicated by the fact that gas is driven into the glass, and can only be recovered by heating strongly.

(9) Hydrogen is driven into glass to a greater extent than nitrogen, and as much as 0.24 c.c. of the former gas has been thus lost during a single experiment.

I wish, in conclusion, to express my indebtedness to Sir William Ramsay, who kindly placed at my disposal the emanation used in the experiments, and whom I have also to thank for his advice and criticism.

UNIVERSITY COLLEGE,
LONDON.

XLV.—*Attempted Resolution of Racemic Aldehydes.*

By WILLIAM ORD WOOTTON.

DURING recent years numerous investigations have been undertaken with a view to elucidating the relationship between the chemical composition and rotatory power of optically active substances. Although considerable progress has been made in this direction by the study of homologous series of ethereal salts and alkyl oxides, it can scarcely be claimed that any generalisations of wide application have yet been established. This is no doubt to be explained partly by the uncertainty attaching to the conventional method of expressing optical rotatory power, and partly by the fact that with few exceptions the compounds chosen for examination have been of too complex a character to admit of great emphasis being laid on the conclusions drawn from them. Owing chiefly to

the difficulty in preparing them, results are wanted with but few structurally simple substances which could be utilised in such work. The ideal substance from this point of view would be an easily accessible compound, of low molecular weight, having only one asymmetric carbon atom, and containing no cyclic grouping; it would be an additional advantage if it contained a chemically reactive group or radicle directly attached to the asymmetric carbon atom, through the agency of which the effect of substitution, addition, or of the introduction of double linkings could be studied. The value of a substance containing a single asymmetric carbon atom in connexion with the application of Guye's modified equation has been pointed out by Bose (*Physikal. Zeitsch.*, 1908, **9**, 860).

The series of aldehydes of the type $\text{CHRR}'\cdot\text{CHO}$ fulfils the foregoing conditions, and since they are easily obtained by the general method of Darzens (*Compt. rend.*, 1904, **139**, 1214), it appeared to be of interest to ascertain whether these presumably racemic substances are capable of resolution into optical antipodes, or whether by other processes they could be obtained in active forms. The direct resolution of racemic aldehydes has been accomplished by Neuberg and Federer (*Ber.*, 1905, **38**, 868), who employed *d*-phenylamylhydrazine, a substance not easy to prepare in the pure state, and which, like most amyl compounds, might be expected to form oily derivatives. In a previous communication (*Trans.*, 1907, **91**, 1890) I have described the preparation of an optically active amine, namely, 4-bromo-3-aminophenyl- α -camphoramic acid, which it was hoped might be applied to the same purpose. The action of this base on hydratropaldehyde, $\text{CHMePh}\cdot\text{CHO}$, has now been examined, but the results obtained did not seem to warrant the extension of its use.

Attention has been drawn (*loc. cit.*) to the difficulty with which camphoric anhydride unites with the nitroanilines to form the nitrophenyl- α -camphoramic acids. This combination has now been effected in the case of *m*-nitroaniline. The nitro-acid obtained has been reduced to the amino-compound, and the behaviour of the product towards a racemic aldehyde studied. For this purpose butylchloral, $\text{CCl}_2\text{Me}\cdot\text{CHCl}\cdot\text{CHO}$, was selected, since Wheeler (*J. Amer. Chem. Soc.*, 1908, **30**, 136) has found that chloral readily condenses with primary aromatic amines, forming well-defined compounds. In the present instance, however, although condensation between one molecule of the aldehyde and two molecule of the base presented no difficulty, it was not found possible to resolve the product by fractional crystallisation into its optically active components.

A more promising method that suggests itself would be to resolve

β , β -substituted camphoric acid by the aid of an alkaloid, and then to decompose the active salts by a mineral acid, when carbon dioxide is eliminated and the aldehyde produced. Experiments have been carried out in this direction, but although a sodium salt of 3-phenyl- β -methylglycidic acid has been obtained having $[\alpha]_D +16.6^\circ$ in aqueous solution, yet the corresponding aldehyde appears to be optically inactive. This, however, may be due to the fact that the acid itself contains two asymmetric carbon atoms, and it is possible that resolution has only been effected in the case of the carbon atom which ceases to be asymmetric on conversion of the acid into the aldehyde:



In the expectation of obtaining optically active bases by the reduction of nitro-derivatives of benzylidenecamphor, I have examined the action of *o*-, *m*-, and *p*-nitrobenzaldehyde on sodium camphor. Although this line of inquiry has been abandoned on account of the very poor yields obtained, the results of the experiments are recorded in the sequel.

A point of some interest has been noticed in connexion with the optical properties of the derivatives of α -camphoramic acid. It has usually been found that the rotatory power of a cyclic compound is considerably greater than that of the corresponding open-chain derivative. Thus the rotatory powers of esters of 1-methyl-3-cyclopentanone-4-carboxylic acid are about thirty times as great as those of the corresponding esters of methyladipic acid (Haller, *Compt. rend.*, 1905, 140, 1205). The hexahydrophthalic acids have much lower specific rotations than their anhydrides (Werner, *Ber.*, 1899, 32, 3046). Many other instances might be quoted. Camphoric acid and its anhydride, however, form an exception to the rule, the acid having $[\alpha]_D +46^\circ$ in alcohol, whilst the anhydride has $[\alpha]_D -7.7^\circ$. Similarly, α -camphoramic acid has $[\alpha]_D +45^\circ$ in acetone, whilst camphorimide has $[\alpha]_D -10.1^\circ$. In order to ascertain whether this peculiarity was exhibited by the *N*-substituted amides and imides of camphoric acid, I have prepared several new members of this series, and determined their rotatory power in acetone solution at a temperature between 19° and 21° . Variations in the concentration of the solution between 1.5 and 3 parts per 100 have very little effect on the rotatory power.

The results are summarised on p. 408.

It will be noticed that the molecular rotatory power of the acid is always greater than that of its corresponding imide, except in the case of the α -naphthyl and *o*-bromophenyl derivatives. The difference between the molecular rotatory powers of the acid and

Derivative.	Camphoramic acid.		Camphorimide.	
	$[\alpha]_D$	$[M]_D$	$[\alpha]_D$	$[M]_D$
Methyl	33.24°	70.6°	7.26°	14.1°
Ethyl	17.1	38.8	8.87	18.5
<i>n</i> -Propyl	18.45	44.5	10.9	24.3
<i>n</i> -Butyl	15.8	40.3	12.8	30.3
<i>n</i> -Amyl	18.9	50.8	7.7	19.3
<i>n</i> -Hexyl	16.9	47.8	10.8	28.6
Allyl	13.54	32.4	7.95	17.6
<i>o</i> -Tolyl	33.9	98.0	15.7	43.0
<i>m</i> -Tolyl	31.0	89.0	17.6	47.0
<i>p</i> -Tolyl	37.0	107.0	12.7	34.0
α -Naphthyl	7.46	24.2	26.34	80.7
β -Naphthyl	64.9	210.9	18.0	55.2
4-Hydroxyphenyl	49.2	143.1	—	—
4-Ethoxyphenyl	39.5	130.0	18.5	55.0
2-Chlorophenyl	-16.4	-60.8	14.1	41.2
3-Chlorophenyl	37.0	114.0	16.2	47.0
4-Chlorophenyl	40.5	125.5	16.2	47.0
2-Bromophenyl	-11.8	-41.8	13.3	44.7
3-Bromophenyl	33.2	117.0	15.4	51.0
4-Bromophenyl	37.8	134.0	15.7	52.0
3-Nitrophenyl	32.0	102.4	1.7	5.1
3-Amino-phenyl	39.9	116.5	—	—
4-Bromo-3-nitrophenyl ..	-48.4	-133.2 *	—	—
4-Bromo-3-aminophenyl ..	40.7	109.5 *	(feebly dextrorotatory)	—
4-Benzeneazophenyl	87.7	332.5 *	—	—

* In alcoholic solution.

imide in the case of *o*-, *m*-, and *p*-isomerides is always greatest in the *p*-compounds. The homologous series of alkyl derivatives show no marked regularity; it is noteworthy, however, that the two allyl compounds show distinctly lower rotatory power than the corresponding *n*-propyl derivatives, in this respect resembling the allylamides in the malic and tartaric series, which show abnormally low rotatory powers when compared with the propylamides (Frankland and Done, Trans., 1906, 89, 1861).

EXPERIMENTAL.

Attempted Preparation of Optically Active Hydratropaldehyde.

Hydratropaldehyde and 4-bromo-3-amino- α -camphoramic acid did not interact in alcoholic solution, either in the cold or on warming, and attempts to obtain a condensation product with benzaldehyde were equally unsuccessful.

Resolution of Sodium β -Phenyl- β -methylglycidate.

Preliminary experiments with the quinine salt of β -phenyl- β -methylglycidic acid having shown that this substance was unsuitable for the purpose, the brucine salt was prepared by adding

brucine hydrochloride (1 mol.), dissolved in the minimum amount of warm water, to a warm aqueous solution of sodium β -phenyl- β -methylglycidate (2 mols.). On allowing the solution to evaporate spontaneously over potassium hydroxide in a vacuum, clusters of radiating, irregular prisms separated, which were crystallised repeatedly from absolute alcohol until optically constant, care being taken to avoid prolonged heating with the solvent:

0.2402 gave 10.4 c.c. N_2 at 23° and 760 mm. $N=4.89$.

$C_{33}H_{36}O_7N_2$ requires $N=4.89$ per cent.

0.6475, in 20 c.c. water, gave, in a 2-dcm. tube, $\alpha=1.14^\circ$, whence $[\alpha]_D -17.7^\circ$.

0.6800, in 20 c.c. absolute alcohol, gave, in a 2-dcm. tube, $\alpha=0.60^\circ$, whence $[\alpha]_D -8.82^\circ$.

When rapidly heated, the salt melts and decomposes at $141-142^\circ$. It decomposes on boiling with water or when heated a few degrees above its melting point, giving brucine and hydratropaldehyde. A good yield of the latter was obtained when the salt was slowly heated under diminished pressure; the product was collected in three separate fractions, but each of these proved to be optically inactive when examined in ethereal or alcoholic solution. The mother liquor remaining from the preparation of the salt was pale brown in colour, and when kept in a vacuum deposited a small quantity of the crystalline brucine salt, together with a resinous substance which appeared to contain hydratropaldehyde together with the free alkaloid. Dilution of the liquid with water caused a further precipitation of brucine. The hydratropaldehyde was found to be inactive.

Sodium d- β -Phenyl- β -methylglycidate, $\begin{matrix} CH_3 \\ C_6H_5 \end{matrix} > C \begin{matrix} CH \cdot CO_2Na \\ O \end{matrix}$, was

obtained by grinding the foregoing brucine salt with water containing the calculated amount of sodium hydroxide. The alkaloid was removed by repeated extraction with chloroform, and the solution allowed to evaporate in a vacuum. The sodium salt was finally obtained in colourless leaflets after three crystallisations from dilute alcohol:

0.3002 gave 0.1097 Na_2SO_4 . $Na=11.88$.

$C_{10}H_9O_3Na$ requires $Na=12.10$ per cent.

0.6000, in 20 c.c. water, gave, in a 2-dcm. tube, $\alpha=1.00^\circ$, whence $[\alpha]_D +16.6^\circ$.

When dissolved in water and treated with slightly less than the calculated amount of sulphuric acid, carbon dioxide was evolved, and the solution became turbid through the separation of hydratropaldehyde. In one experiment this was removed by steam dis-

tillation, and in another by extraction with ether. Both specimens, however, appeared to be optically inactive when examined in 5 per cent. solutions of alcohol, chloroform, or ether. The aldehyde, moreover, gave a semicarbazone identical with that obtained from the racemic sodium salt.

Attempted Resolution of Butylchloral.—Condensation occurs readily when an aqueous solution of *m*-aminophenyl- α -camphoramic acid (see below) is shaken with butylchloral. It is advisable, however, to add the butylchloral (1 mol.) to a solution of the sodium salt of the acid (2 mols.). The aldehyde dissolves immediately with considerable development of heat.

Trichlorobutylidenebis-3-aminophenyl- α -camphoramic Acid,
 $\text{CMeCl}_2\cdot\text{CHCl}\cdot\text{CH}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}_2\text{H})_2$

separates as a bulky mass of colourless needles when the solution of its sodium salt is acidified with acetic acid. After crystallisation from dilute alcohol, it melts and decomposes at $126-130^\circ$ when heated moderately rapidly. Attempts to resolve it by fractional crystallisation from this solvent and also from acetone were not successful, successive fractions showing practically the same rotatory power. Prolonged heating with solvents brings about decomposition:

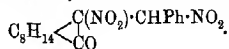
0.9081 gave 0.0510 AgCl. $\text{Cl}=13.89$.

$\text{C}_{38}\text{H}_{47}\text{O}_6\text{N}_4\text{Cl}_3$ requires $\text{Cl}=14.38$ per cent.

0.5110, in 20 c.c. acetone, gave, in a 2-dm. tube, $\alpha_D +1.40^\circ$, whence $[\alpha]_D +27.4^\circ$.

Nitro-derivatives of Benzylidenecamphor.

The only nitro-derivative of benzylidenecamphor hitherto known has been described by Haller (*Compt. rend.*, 1895, **121**, 36). By the action of fuming nitric acid on benzylidenecamphor, a colourless compound was obtained, to which he ascribed the constitution:



The nitro-groups do not appear to be attached to the benzene nucleus, since the substance furnishes benzylidenecamphor on reduction.

Action of p-Nitrobenzaldehyde on Sodium Camphor.—The sodium camphor required in these experiments was prepared by the action of sodium or finely divided sodamide on camphor dissolved in dry ether, benzene, or toluene. The reactions appeared to follow the same course whichever method was adopted, the use of sodamide with ether, however, was preferred as giving cleaner products and

a better yield. On adding two-thirds of the calculated quantity of *p*-nitrobenzaldehyde to a well-cooled suspension of sodium camphor, a vigorous action ensued, accompanied by development of heat. The mixture was kept below 5° for an hour, and then heated for a short time on the water-bath. The reddish-brown, pasty mass was extracted with water, the layer of organic solvent separated, dried, and finally heated on the water-bath until the solvent and the greater part of unaltered camphor had been removed. The aqueous extract on the addition of an acid gave a voluminous yellow precipitate consisting chiefly of *p*-nitrobenzoic acid. The residue left after evaporation of the organic solvent appeared as a viscous, red oil, which slowly deposited yellow crystals. The oily matter was removed by extraction with cold alcohol and examined separately. The crystalline residue contained the following two substances.

I. A compound, $C_{34}H_{38}O_4N_2$.—This product is sparingly soluble in alcohol, ether, or benzene, and readily so in pyridine or carbon tetrachloride, from which it separates in small, orange-red prisms, melting at 280–281°. The compound is distinguished by its remarkably high rotatory power; it does not give Liebermann's reaction, and develops no coloration with alcoholic potash. Two determinations of the molecular weight in chloroform solution by the ebullioscopic method gave 422 and 446 respectively, the above formula requiring 538:

0.0913 gave 0.2529 CO_2 and 0.0597 H_2O . $C=75.52$; $H=7.25$.

0.3559 „ 12.8 c.c. N_2 at 18° and 744 mm. $N=5.65$.

$C_{34}H_{38}O_4N_2$ requires $C=75.82$; $H=7.06$; $N=5.20$ per cent.

0.0939, in 25 c.c. chloroform, gave, in a 2-dm. tube, $\alpha_D +4.55^\circ$, whence $[\alpha]_D +605^\circ$, and $[M]_D +3255^\circ$.

II.—4-Nitrobenzylidenecamphor, $C_{20}H_{24}O_2$.—This

compound separates from alcohol in bright yellow, glistening leaflets, melting at 156–157°; it is sparingly soluble in alcoholic potassium hydroxide, giving a yellow solution. Concentrated sulphuric acid develops an orange-red coloration:

0.1012 gave 0.3148 CO_2 and 0.0592 H_2O . $C=71.71$; $H=6.38$.

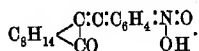
0.1780 „ 7.6 c.c. N_2 at 16° and 754 mm. $N=4.82$.

$C_{20}H_{24}O_2$ requires $C=71.59$; $H=6.66$; $N=4.88$ per cent.

0.3102, in 20 c.c. chloroform, gave, in a 2-dm. tube, $\alpha_D +3.55^\circ$, whence $[\alpha]_D +437^\circ$, and $[M]_D +1345^\circ$.

Examination of the Alcoholic Extract.—A deep red oil, having a slight odour of camphor, remained after removal of the alcohol by evaporation. The oil is insoluble in water, but freely soluble in the usual organic media; on adding alkali hydroxide to its alcoholic solution, an intense purple coloration is developed, which, on

dilution with water, changes to red. The colour is destroyed by acids, but restored by alkalis. It is possible that this product contains an enolic form of 4-nitrobenzylidenecamphor:



A chromophoric oil having similar properties has been described by Forster, who obtained it by the action of *p*-nitrobenzyl chloride on isonitrosocamphor in presence of sodium ethoxide (Trans., 1908, 93, 249). Decomposition occurs when the oil is distilled under diminished pressure, and all attempts to isolate a pure compound or prepare a crystalline derivative have failed.

No chromophoric substance is formed if the temperature of reaction is allowed to rise during the preparation; under these conditions, the main product is the compound $\text{C}_{34}\text{H}_{38}\text{O}_4\text{N}_2$, together with a very insoluble brown substance which has not yet been obtained in a state of purity. To ascertain whether the presence of the camphor nucleus is essential for its formation, experiments have been carried out on the action of *p*-nitrobenzaldehyde on the sodium derivatives of ethyl acetoacetate, carvone, and pulegone; no chromophoric product was recognised, however, and this would appear to exclude the possibility of the colour having arisen from the action of the alkali on any derivative of dinitrostilbene. It may be mentioned that the sodium derivative of pulegone is very readily prepared by the action of sodamide on an ethereal solution of pulegone. The action proceeds briskly without warming, and a good yield is obtained.

Action of o- and m-Nitrobenzaldehyde on Sodium Camphor.

2-Nitrobenzylidenecamphor, $\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}$, prepared in the same way as the 4-nitro-compound, occurs as well-formed, light brown prisms, melting at 116—117°. A solution in chloroform gave $[\alpha]_D^{20} +50^\circ$ approximately; owing to the absorption of light, the rotatory power could not be accurately determined. The compound itself gives no coloration with alcoholic potassium hydroxide, but the oily material from which it is separated develops an intense purple coloration with this reagent:

0.2633 gave 11.9 c.c. N_2 at 28° and 766 mm. $\text{N}=4.99$.

$\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}$ requires $\text{N}=4.88$ per cent.

3-Nitrobenzylidenecamphor, $\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}$.—This compound and *m*-nitrobenzoic acid are the only products of the action of *m*-nitrobenzaldehyde on sodium camphor. It was obtained as a yellow oil, which, on addition of alcohol, rapidly solidified. When

crystallised from hot alcohol, it forms very pale yellow needles, melting at 110—111°.

0.2024 gave 9.4 c.c. N_2 at 19° and 748 mm. $N=5.13$.

$C_{17}H_{19}O_3N$ requires $N=4.88$ per cent.

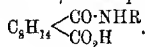
0.0934, in 15 c.c. chloroform, gave, in a 2-dcm. tube, $\alpha_D +3.92^\circ$, whence $[\alpha]_D +311^\circ$, and $[M]_D +783^\circ$.

Alkyl Derivatives of α -Camphoramic Acid, $CO_2H \cdot C_8H_{14} \cdot CO \cdot NHR$.

The following new members of the series were prepared by the interaction of camphoric anhydride (1 mol.) with an alcoholic solution of the amine (2 mols.). After purification by conversion into the sodium salt, the free acid was regenerated by the addition of hydrochloric acid and crystallised from dilute acetone:

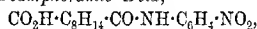
Derivative.	Empirical formula.	Crystalline form.	M. p.	Analysis.	
				Found.	Theory, per cent.
Ethyl	$C_{12}H_{21}O_3N$	Hexagonal leaflets	173—175°	$N=6.08$	6.17
n-Propyl...	$C_{13}H_{23}O_3N$	Hexagonal leaflets	187—188	$N=5.79$	5.81
n-Butyl	$C_{14}H_{25}O_3N$	Hexagonal leaflets	124—125	$C=85.71$ $H=9.48$	65.89 9.80
n-Amyl	$C_{15}H_{27}O_3N$	Crystalline mass	—	$C=86.58$ $H=10.25$	66.91 10.03
n-Hexyl	$C_{16}H_{29}O_3N$	Hexagonal leaflets	123—124	$N=5.21$	4.95
Allyl	$C_{13}H_{21}O_3N$	Leaflets	157—158	$N=5.66$	5.87

Aryl Derivatives of α -Camphoramic Acid,



In most cases these compounds are readily obtained by heating an intimate mixture of camphoric anhydride and the substituted amine for a few minutes at 150—180°. In the case of *m*-nitro-aniline, *a*-naphthylamine, and ortho-substituted amines, it is necessary to heat for a longer period in sealed tubes.

3-Nitrophenyl- α -camphoramic Acid,



is prepared by heating 13 grams of camphoric anhydride with 10 grams of *m*-nitroaniline at 150° for one hour in a sealed tube. The crystalline mass is dissolved in dilute ammonia, the solution filtered after twenty-four hours, and then acidified. The first few drops of acid precipitate a brown, resinous product, but further addition of acid yields the required compound in a state of purity. It is crystallised from acetic acid containing a little stannous chloride, and finally from alcohol, from which it separates in large,

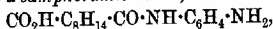
colourless, hexagonal leaflets, which darken at about 200°, and melt and decompose at 212–213°.

0.3052 gave 18.6 c.c. N_2 at 20° and 754 mm. $N=8.71$.

$C_{16}H_{20}O_5N_2$ requires $N=8.75$ per cent.

0.6178, in 20 c.c. acetone, gave, in a 2-dm. tube, $\alpha_D +1.97^\circ$, whence $[\alpha] +32.0^\circ$.

3-Aminophenyl- α -camphoramic Acid,



prepared from the foregoing compound by reduction with ferrous sulphate in ammoniacal solution, forms small, colourless needles, melting at 196–197°:

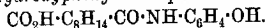
0.2000 gave 16.6 c.c. N_2 at 21° and 766 mm. $N=9.53$.

$C_{16}H_{22}O_5N$ requires $N=9.65$ per cent.

0.3908, in 20 c.c. acetone, gave, in a 2-dm. tube, $\alpha_D +1.56^\circ$, whence $[\alpha]_D +39.9^\circ$.

The acetyl derivative crystallises in silky needles, melting at 220–221°. The hydrochloride of the base is easily soluble in water, and on diazotisation yields a clear solution which, on the addition of alkaline β -naphthol, furnishes a bright red azo-compound. A solution of the base in dilute alcohol gives an immediate precipitate on the addition of an aldehyde; this arises from condensation of two molecules of the base with one of the aldehyde.

4-Hydroxyphenyl- α -camphoramic Acid,



A brisk reaction occurs when camphoric anhydride and *p*-aminophenol are heated together. The dark-coloured product contains small quantities of a substance characterised by the intense purple coloration developed with aqueous alkali hydroxides; it was crystallised from alcohol until the mother liquor no longer showed this reaction. Recrystallisation from acetic acid, after treatment with animal charcoal, gave small, pale brown prisms. The melting point was somewhat indefinite, the compound sintering at 236° and decomposing at 250°. The product after fusion dissolved in aqueous alkalis, giving deep purple solutions, probably owing to the formation of a phthalein:

0.0986 gave 0.2385 CO_2 and 0.0648 H_2O . $C=65.80$; $H=7.30$.

$C_{16}H_{21}O_4N$ requires $C=65.98$; $H=7.22$ per cent.

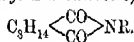
0.3641, in 20 c.c. acetone, gave, in a 2-dm. tube, $\alpha_D +1.80^\circ$, whence $[\alpha]_D +49.16^\circ$.

The following aryl derivatives of α -camphoramic acid were also prepared:

Analysis.

Derivative.	Empirical formula.	Crystalline form.	M. p.	Found.	Theory, per cent.
<i>o</i> -Tolyl	$C_8H_9O_2N$	Long needles	194—196°	N=4.72	4.84
<i>m</i> -Tolyl	$C_9H_9O_2N$	Needles	206—209	N=4.76	4.84
<i>p</i> -Tolyl	$C_9H_9O_2N$	Leaflets	212—214	N=4.96	4.84
<i>α</i> -Naphthyl	$C_{10}H_9O_2N$	Needles	233—235	N=4.31	4.31
<i>β</i> -Naphthyl	$C_{10}H_9O_2N$	Lustrous leaflets	210—212	N=4.68	4.31
4-Ethoxyphenyl ...	$C_{10}H_{11}O_3N$	Long needles	185—187	N=4.35	4.39
2-Chlorophenyl ...	$C_8H_7O_2NCl$	Minute crystals	139—140	Cl=11.22	11.47
3-Chlorophenyl ...	$C_8H_7O_2NCl$	Leaflets	207—209	Cl=11.35	11.47
4-Chlorophenyl ...	$C_8H_7O_2NCl$	Prisms	192—194	Cl=11.38	11.47
2-Bromophenyl ...	$C_8H_7O_2NBr$	Vitreous mass	about 78	Br=22.42	22.60
3-Bromophenyl ...	$C_8H_7O_2NBr$	Small tablets	215—217	Br=22.54	22.60

* This compound, together with the corresponding imide, has recently been described by Abati and Notaris (*Gazzetta*, 1909, 39, ii, 219). These authors give the melting point 201—209° for the acid and 131° for the imide.

N-Alkyl and Aryl Derivatives of Camphorimide,

By boiling a solution of a *N*-substituted α -camphoramic acid in glacial acetic acid with acetyl chloride for two hours, and pouring the liquid into excess of dilute ammonia, the corresponding imide is obtained in almost theoretical yield. The following were prepared:

Derivative.	Empirical formula.	Crystalline form.	M. p.	Analysis.	
				Found.	Theory, per cent.
<i>n</i> -Propyl	$C_{13}H_{21}O_2N$	Prisms	40—41°	C=69.92 H=9.37	69.95 9.42
<i>n</i> -Butyl	$C_{14}H_{23}O_2N$	Lath-like crystals	61—62	N=6.13	5.91
<i>n</i> -Amyl	$C_{15}H_{25}O_2N$	Oil	—	N=5.50	5.58
<i>n</i> -Hexyl	$C_{16}H_{27}O_2N$	Oil	—	N=5.31	5.28
<i>o</i> -Tolyl	$C_9H_9O_2N$	Long needles	195—196	N=5.21	5.16
<i>m</i> -Tolyl	$C_9H_9O_2N$	Glistening leaflets	117—118	N=5.27	5.16
<i>p</i> -Tolyl	$C_9H_9O_2N$	Flat prisms	127—128	C=74.98 H=7.61	75.26 7.75
<i>α</i> -Naphthyl	$C_{10}H_9O_2N$	Stout prisms	211—212	N=4.68	4.66
<i>β</i> -Naphthyl	$C_{10}H_9O_2N$	Small needles	197—198	N=4.57	4.56
2-Chlorophenyl ...	$C_8H_7O_2NCl$	Flat prisms	125—126	Cl=11.97	12.18
3-Chlorophenyl ...	$C_8H_7O_2NCl$	Needles	172—173	Cl=12.03	12.18
4-Chlorophenyl ...	$C_8H_7O_2NCl$	Prisms	162—163	N=4.89	4.80
2-Bromophenyl ...	$C_8H_7O_2NBr$	Small prisms	139—140	Br=23.57	23.80
3-Bromophenyl ...	$C_8H_7O_2NBr$	Needles	184—185	Br=23.68	23.80
3-Nitrophenyl	$C_8H_7O_4N_2$	Rhombohedral prisms	146—147	N=8.97	9.27

ROYAL COLLEGE OF SCIENCE,
SOUTH KENSINGTON, S.W.

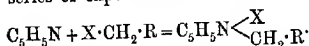
XVI.—The Relation between Reactivity and Chemical Constitution of Certain Halogen Compounds.

By HANS TRACHER CLARKE.

THE reactivity of the halogens in organic halogen compounds has been studied by various investigators: Wislicenus (*Annalen*, 1882, **212**, 239), with ethyl sodioacetoacetate; Hecht, Conrad, and Brückner (*Zeitsch. physikal. Chem.*, 1889, **4**, 273), with sodium ethoxide; Menshutkin (*Zeitsch. physikal. Chem.*, 1890, **5**, 589), with triethylamine; Burke and Donnan (*Trans.*, 1904, **85**, 555; *Zeitsch. physikal. Chem.*, 1909, **69**, 148), with silver nitrate; Slator (*Trans.*, 1904, **85**, 1286; 1905, **87**, 482), Slator and Twiss (*Trans.*, 1909, **95**, 93), with sodium thiosulphate; Senter (*Trans.*, 1907, **91**, 460; 1909, **95**, 1827), with water and with alkalis; but no definite conclusions appear to have been drawn as to the relations between reactivity and constitution.

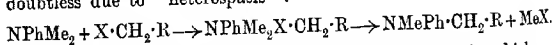
The present paper deals with compounds of the type $X \cdot CH_2 \cdot R$, the object being to study the influence of the nature of the group (R) on the reactivity of the halogen (X).

The reactivity was determined by the measurement of the velocity of the reaction between pyridine and the halogen compound in absolute alcoholic solution, identical conditions being observed throughout the series of experiments:



From the scheme representing the reaction, it is evident that ionic reactions are improbable.

Attempts were at first made with ethylaniline and dimethylaniline at the temperature of boiling alcohol, but it was found that the values of "K" calculated for a bimolecular reaction, decreased with the progress of the reaction, this effect being doubtless due to "heterospasis":



Pyridine was accordingly selected as a tertiary base in which no such decomposition could occur. Moreover, as pyridine is more strongly basic than the above-mentioned derivatives of aniline, the reaction could take place with measurable velocity at a lower temperature.

Equal volumes of *N*/2-solutions of pyridine and the halogen compound were mixed and maintained at the temperature of 55.6°, afforded by a water-bath surrounded with boiling acetone

under constant pressure, aliquot portions being withdrawn at intervals and the ionised halogen titrated with silver nitrate. The constant was calculated from the usual formula for a bimolecular reaction, namely:

$$K = \frac{1}{C_0 \cdot t} \cdot \frac{C_t}{C_0 - C_t}$$

In nearly every case the values of K did not vary from those required for a bimolecular reaction by more than experimental error.

The experimental results are set forth in the following table; they will be discussed in detail on subsequent pages:

	X.	R.	K.
n-Propyl bromide	Br·CH ₂	Et	0·0179
Allyl "	Br·CH ₂	CH:CH ₂	1·253
Benzyl "	Br·CH ₂	Ph	5·118
Cinnamyl "	Br·CH ₂	CH:CH·Ph	0·472
Bromoacetic acid	Br·CH ₂	CO ₂ H	0·666
Methyl bromoacetate	Br·CH ₂	CO ₂ Me	0·919
Ethyl "	Br·CH ₂	CO ₂ Et	1·004
n-Propyl "	Br·CH ₂	CO ₂ Pr ^a	0·752
iso-Propyl "	Br·CH ₂	CO ₂ Pr ^b	1·048
n-Butyl "	Br·CH ₂	CO ₂ ·CH ₂ ·CH ₂ ·Et	0·770
tert.-Butyl "	Br·CH ₂	CO ₂ ·CMe ₃	0·934
Phenyl "	Br·CH ₂	CO ₂ Ph	1·927
Benzyl "	Br·CH ₂	CO ₂ ·CH ₂ ·Ph	1·211
Allyl "	Br·CH ₂	CO ₂ ·C ₃ H ₅	0·768
Ethyl β-bromopropionate	Br·CH ₂	CH ₂ ·CO ₂ ·Et	0·0277
Bromoacetal	Br·CH ₂	CH(OEt) ₂	0·012
Chloroacetamide	Cl·CH ₂	CO·NH ₂	0·01115
Chloroacetanilide	Cl·CH ₂	CO·NHPh	0·0264
Bromoacetanilide	Br·CH ₂	CO·NHPh	1·533
Diphenylchloroacetamide	Cl·CH ₂	CO·NHPh ₂	0·0341
Chloroacetone	Cl·CH ₂	CO·Me	0·0686
Chloroacetophenone	Cl·CH ₂	CO·Ph	0·1339
Bromoacetophenone	Br·CH ₂	CO·Ph	7·269

The first fact established was that in a compound of the type X·CH₂·R the reactivity of the halogen, as determined by the above method, was controlled by the residual affinity of the atom or group (R) directly attached to the methylene carbon atom. The following series will illustrate this conclusion:

	K.
n-Propyl bromide	0·0179
Methyl bromoacetate.....	0·919
Allyl bromide.....	1·253
Benzyl "	5·118

Monochloromethyl ether and bromonitromethane were also examined. In both these cases there are present groups to which a large amount of residual affinity is attributable (OMe; NO₂). Chloromethyl ether reacted so rapidly with alcoholic pyridine that no measurement could be obtained; whereas bromo-

nitromethane formed a pyridine salt at once, and very little elimination of bromine ensued.

Taking, then, this rule as a basis, an attempt has been made to determine the degree of unsaturation in various compounds of this type in order to elucidate the nature of the different groups involved.

The effect of conjugation of a phenyl nucleus with an ethenoid linking appears to diminish the total residual affinity inherent in the carbon atom in the α -position with respect to the methylene group, the reactivity of cinnamyl bromide being less than one-half of that of allyl bromide:

Cinnamyl bromide	$\text{Ph}\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\text{Br}$	$K=0.473$
Allyl "	$\text{CH}_2=\text{CH}\cdot\text{CH}_2\text{Br}$	$K=1.253$

Turning now to the derivatives of chloro- and bromo-acetic acids, it was found that the reactivity of the halogen varied with the nature of the radicle to which the halogen-acyl group was attached.

When equimolecular quantities of pyridine and bromoacetic acid were mixed in alcoholic solution, it was found, contrary to expectation, that elimination of bromine took place along the lines of a bimolecular reaction. This fact would tend to point to the absence of stable salt-formation in absolute alcohol:

Bromoacetic acid	$K=0.666$
------------------------	-----------

The reactivity of the halogen in the following series of saturated aliphatic esters was examined:

	K .		K .
Methyl bromoacetate	0.919	isoPropyl bromoacetate	1.048
Ethyl "	1.004	n-Butyl "	0.770
n-Propyl "	0.752	tert.-Butyl "	0.934

The phenyl, benzyl, and allyl esters of bromoacetic acid were examined in the same manner:

	K .
Phenyl bromoacetate	1.327
Benzyl "	1.211
Allyl "	0.768

In phenyl bromoacetate, which exhibits a greatly exalted reactivity, the alcoholic radicle contains the greatest residual affinity. In benzyl bromoacetate, in which a methylene group is interposed between the phenyl and the bromoacetoxyl groups, the effect still persists, although considerably diminished. The reactivity of the allyl ester, when compared with that of the *n*-propyl ester, shows a slight exaltation—to a less extent, however, owing to the less powerful influence of the ethenoid as compared with the benzenoid grouping.

Since the values obtained from allyl bromoacetate and benzyl

bromoacetate indicate that the influence of the unsaturated group is appreciable even when situated in the β -position, the reactivity of ethyl β -bromopropionate was measured:

Ethyl β -bromopropionate $K=0.0277$

This value, when compared with the saturated standard, *n*-propyl bromide ($K=0.0179$), is sensibly exalted. Bromoacetal, on the other hand, yields a value ($K=0.012$) which shows the reactivity of the halogen to be slightly depressed.

In the series of halogen-acetylammides, the reactivity of the halogen compounds was measured:

	K .		K .
Chloroacetamide	0.01115	Bromoacetanilide	1.533
Chloroacetanilide	0.0264	Diphenylchloroacetamide..	0.0341

In the case of the halogen-acetanilides, the reactivity constant of the bromine derivative is 58.1 times as great as that of the chlorine derivative. Taking this ratio, the value calculated from chloroacetamide yields $K=0.648$ for bromoacetamide, a substance difficult to obtain in a high state of purity, and, moreover, insufficiently soluble in alcohol.

The same rule thus holds good for the $\text{Br}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}\cdot$ and the $\text{Br}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{N}\cdot$ structures, the replacement of hydrogen by phenyl giving rise to increased reactivity of the halogen, as the following table shows:

	K .		K .
Bromoacetic acid.....	0.666	(Bromoacetamide	0.648)
Phenyl bromoacetate	1.927	Bromoacetanilide	1.533

The reactivities of halogenated ketones were found to be greatly in excess of those of the corresponding carboxylic compounds enumerated above:

	K .
Chloroacetone	0.0686
Chloroacetophenone	0.1339
Bromoacetophenone	1.269

from which the constant for bromoacetone can be calculated, being approximately $K=3.720$. In the case of the ketones, as in the case of bromoacetic esters, the replacement of a methyl group by a phenyl group occasions approximately doubled reactivity.

Two series of measurements were carried out in an aqueous-alcoholic solution (25 c.c. absolute alcohol diluted to 100 c.c. with water), the substances examined being methyl bromoacetate and potassium bromoacetate, and the initial concentration of the reacting substances $N/4$ before mixing:

	K .
Methyl bromoacetate	14.61
Potassium „	9.07

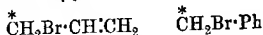
It will be observed that a far greater velocity of reaction ensued in the presence of water than in absolute alcohol. The ratio between the constants obtained for these substances in aqueous alcoholic solution is of the same order as that between those obtained for methyl bromoacetate and for bromoacetic acid in alcoholic solution:

Methyl bromoacetate (0.919) :	bromoacetic acid (0.666) =	1 : 0.775
" " (14.61) :	potassium bromoacetate (9.07) =	1 : 0.621

It would thus appear that no radical change in constitution occurs during salt-formation and esterification.

Discussion of Results.

The author inclines to regard the variation of the reactivity of the halogen in compounds containing unsaturated groups in the 3-position as due to the weakening of the bonds attached to the α -carbon atom caused by the strengthening of the bond between the unsaturated group and the α -carbon atom. To take the case of allyl bromide and benzyl bromide, all residual affinity of the methylene carbon atom (*):



is absorbed by the unsaturated group, leaving the remaining three atoms less strongly attached to the carbon atom. This is borne out by the observation of Wislicenus (*loc. cit.*) that the halogen vinyl iodide ($\text{CH}_2:\text{CH}\cdot$) is subnormally reactive. The subnormal reactivity of the halogens in aryl halides may perhaps be due to the same cause. This view of the variable strength of affinities with varying substituents has already been put forward by Claus (*Ber.*, 1881, 14, 432), and fully discussed by Werner and by Flürscheim.

Of the compounds containing the halogen-acetyl grouping, the greatest reactivity of the halogen is to be found among the ketones. This tends to show that the ketonic carbonyl group possesses more residual affinity than the carboxylic and carbamidic carbonyl group. It has long been suspected that in the carboxyl group the two oxygen atoms exert some mutual attraction, and in a recent publication Miss Smedley (*Trans.*, 1909, 95, 231) has assigned to the carboxyl group a constitution, $\cdot\text{C}\begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix}$, in which the third

and fourth valencies of the two oxygen atoms are united.

Now, it was shown above that in the case of phenyl bromoacetate the reactivity of the halogen is approximately double that of the corresponding methyl ester, and this fact indicates that some influence must be at work which transmits the effect through a series of atoms so as to exalt the reactivity of the halogen.

Hitherto, the formulation of the carboxyl group has been essentially of a static nature. The old formula, $\cdot\text{C}\begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$, must be discarded, since it furnishes no distinction between the carboxylic and ketonic carbonyl groups, and the formula advocated by Goldschmidt (*Zeitsch. Elektrochem.*, 1904, 10, 221), $\cdot\text{C}:\text{O}:\text{O}\cdot$, is difficult to reconcile with the chemical and physical properties of the group.

Miss Smedley's view of the constitution of the carboxyl group is in harmony with the results above mentioned, except in so far that its static nature gives no explanation of the variations in reactivity due to differences in the alcoholic radicle. The author therefore suggests that this formulation should be modified in such a way that the greater or less unsaturated character of the carbonyl group is expressed.

There are two possible methods of regarding the problem. The first is that the bond between the oxygen atoms is variable in intensity, resulting in a formula of this nature: $\cdot\text{C}\begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$; the

second being that while the attraction between the oxygen atoms remains constant, the bond between the hydroxylic oxygen atom and the carbon atom varies in intensity, requiring a formula of the

type $\cdot\text{C}\begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$. Considering the problem as a whole, the evidence tends to favour the first view.

A comparison of the conditions obtaining in methyl bromoacetate and phenyl bromoacetate may serve to illustrate this interpretation:



In the phenyl ester a greater proportion of the residual affinity of the hydroxylic oxygen atom is absorbed by the phenyl group than in the case of the methyl ester, so that the attraction between the oxygen atoms is lessened. A more unsaturated or, it might be said, a more ketonic form of carbonyl is thus produced, with consequent increase of reactivity of the bromine atom.

A similar structure may be applied to the amides: $\cdot\text{C}\begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{N} \end{smallmatrix}$.

Replacement of the amidic hydrogen atoms by groups rich in residual affinity, such as phenyl, enhances the ketonic character of the carbonyl group.

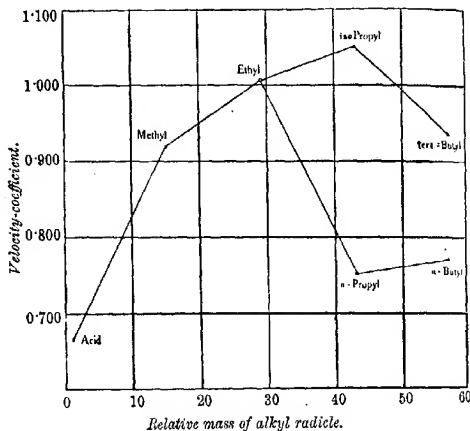
The variations observed through the series of aliphatic esters

which were examined are interesting, and point to differences in residual affinity of the several alkyl groups.

The free acid is less reactive than any of the esters, whilst the reactivity increases from the methyl ester through the ethyl ester to the isopropyl ester, that is, on successive substitution of the hydrogen atoms of the methyl group. Slator (*Trans.*, 1905, 87, 481) also has found that ethyl bromoacetate is more reactive towards sodium thiosulphate than methyl bromoacetate. The reactivity of the tertiary butyl ester, however, falls to a value approximating that of the methyl ester.

On continuing substitution in a normal chain, the reactivity of

FIG. 1.



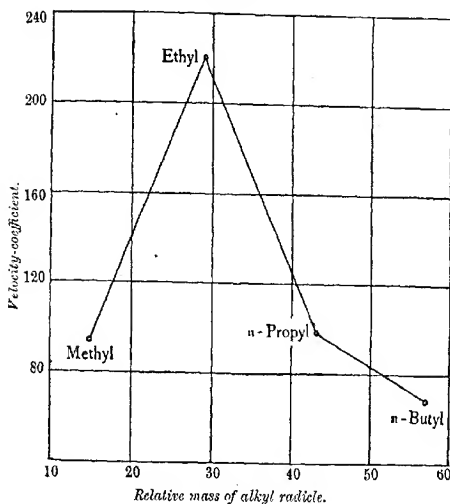
the *n*-propyl ester falls to a strikingly low value, rising again slightly in the case of the *n*-butyl ester. Thus, both the butyl esters examined display anomalous reactivity, breaking the continuity of the curves. The curve furnished by the normal esters, however, perhaps displays the periodic rise and fall observed in many of the physical properties of homologous series.

It may here be mentioned that these results are strictly comparable, as steric considerations can play no part in the elimination of bromine from bromoacetic esters.

The results found by Burke and Donnan (*loc. cit.*) for the reactivities of the alkyl iodides produce a curve, which, while similar in appearance, leads to the opposite conclusion. The

author's results tend to show that the residual affinity of the normal series of alkyl groups rises from methyl to ethyl, and falls to *n*-propyl, rising again slightly to *n*-butyl. On the other hand, since the halides of groups rich in residual affinity, such as phenyl or vinyl, have been shown to be distinctly sluggish towards halogen eliminating agents, it would follow from the work of Burke and Donnan that the residual affinity would be at a minimum in the ethyl radicle, increasing towards methyl on the one hand, and towards *n*-propyl and *n*-butyl on the other. A satisfactory explanation remains yet to be put forward to account for the discordant results.

FIG. 2.



obtained for reaction velocity measurements in so far as the alkyl groups are concerned.

With regard to the variations in reactivity due to the structure of the alkyl radicles, no influence ascribable to "alkylene" or "alkylidene" dissociation (Nef, *Annalen*, 1899, **309**, 126) can be at work, dissociation of this type being highly improbable in carboxylic esters.

The measurements carried out with methyl bromoacetate indicate that the reaction with pyridine takes place with far greater velocity in aqueous alcohol than in absolute alcoholic solution. Slator and

Twiss (Trans., 1909, 96, 99), on the other hand, and that sodium thiosulphate reacts more rapidly with methyl iodide and with chloroacetone in aqueous-alcoholic solution than in pure water.

In the halogen acetic acids and their derivatives, the influence between the halogen atom and the carboxyl group may be regarded as mutual, since Lichty (*Amer. Chem. J.*, 1895, 17, 27) has shown that the initial velocities of esterification of chloro- and bromo-acetic acids by ethyl alcohol are greater than that of acetic acid. Lichty has also shown (*Annalen*, 1902, 319, 369) that the initial esterification velocity and affinity constants of the α -halogen-fatty acids greatly exceed those of the β - and γ -halogen-fatty acids. This is in entire harmony with the decreased reactivity of the bromine in ethyl β -bromopropionate as compared with ethyl bromoacetate.

EXPERIMENTAL.

The substances employed for the reactivity measurements were in most cases purchased from Kahlbaum, or prepared by standard methods. Semi-normal solutions of pyridine and the various halogen compounds in absolute alcohol were prepared, 50 c.c. of each solution being mixed and maintained at 55.6°. At definite intervals of time, 10 c.c. were withdrawn and titrated with standard silver nitrate (approximately $N/10$), the pipettes being standardised for the temperature. In some cases, potassium chromate was used as an indicator, in others, Volhard's thiocyanate method was employed to determine the end-point. The 10 c.c. of solution were added to about 100 c.c. of cold distilled water, covered, when the substances were highly reactive, with a layer of ether to remove the unchanged halogen compounds from the action of the silver nitrate.

The following measurements were carried out in absolute alcoholic solution; temperature 55.6°; initial concentration $N/4$; t represents the time-interval in hours, C_t the percentage decomposition, and K the velocity-coefficient:

n-Propyl Bromide.

t	0.000	16.750	19.500	21.584	24.000
C_t	0.00	6.80	8.00	8.80	9.80
K	—	0.0174	0.0182	0.0179	0.0181

Mean value of $K=0.0179$.

Allyl Bromide.

t	0.000	1.000	1.333	2.333	2.500	3.000
C_t	0.00	23.80	29.58	42.50	43.79	48.80
K	—	1.248	1.258	1.268	1.246	1.245

Mean value of $K=1.253$.

Benzyl Bromide.

t	0.000	0.500	0.667	0.834	1.000	1.167
C_t	0.00	39.55	46.47	50.91	56.11	60.05
K	—	5.231	5.209	4.978	5.022	5.150

Mean value of $K=5.118$.

Cinnamyl Bromide.

t	0.000	0.167	0.767	1.917	3.250	
C_t	0.00	1.97	8.27	18.51	27.59	
K	—	0.482	0.471	0.475	0.469	

Mean value of $K=0.472$.

Bromoacetic Acid.

t	0.000	0.684	1.033	1.333	1.500	1.667	1.833
C_t	0.00	9.00	14.60	18.40	20.00	21.60	24.00
K	—	0.642	0.662	0.676	0.667	0.660	0.688

Mean value of $K=0.666$.

Methyl Bromoacetate.

t	0.000	1.000	1.500	3.000	3.500	4.000	4.500
C_t	0.00	18.43	25.72	41.09	45.30	47.21	50.66
K	—	0.904	0.923	0.930	0.948	0.894	0.914

Mean value of $K=0.919$.

Ethyl Bromoacetate.

t	0.000	1.000	2.000	3.000	4.000	4.500	5.000	6.000
C_t	0.00	20.00	33.80	43.40	50.52	53.00	55.32	57.60
K	—	1.000	1.021	1.022	1.021	1.003	0.991	0.988

Mean value of $K=1.004$.

n-Propyl Bromoacetate.

t	0.000	1.500	2.500	3.584	4.500	
C_t	0.00	22.07	31.91	40.40	45.60	
K	—	0.755	0.750	0.757	0.744	

Mean value of $K=0.752$.

isoPropyl Bromoacetate.

t	0.000	1.000	1.500	2.000	2.500	3.000
C_t	0.00	20.88	27.97	34.67	39.40	44.11
K	—	1.055	1.030	1.060	1.040	1.053

Mean value of $K=1.048$.

n-Butyl Bromoacetate.

t	0.000	1.333	2.000	2.500	3.000
C_t	0.00	20.09	28.36	32.30	36.02
K	—	0.754	0.792	0.764	0.771

Mean value of $K=0.770$.

tert.-Butyl Bromoacetate.

<i>t</i>	0.000	1.000	1.800	2.250	2.500
<i>C_t</i>	0.00	19.00	29.90	34.40	36.80
<i>K</i>	—	0.938	0.938	0.932	0.932

Mean value of $K=0.934$.*Phenyl Bromoacetate.*

<i>t</i> ...	0.000	0.433	0.600	0.767	0.934	1.100	1.267	1.433	1.600
<i>C_t</i> ...	0.00	17.28	22.28	27.28	31.11	34.95	37.67	41.70	43.40
<i>K</i> ...	—	1.929	1.911	1.958	1.936	1.963	1.907	1.915	1.919

Mean value of $K=1.927$.*Benzyl Bromoacetate.*

<i>t</i>	0.000	0.784	1.000	1.333	1.584	2.350	2.817	3.000
<i>C_t</i>	0.00	18.71	22.83	28.95	32.60	42.55	46.10	47.29
<i>K</i>	—	1.174	1.180	1.244	1.204	1.263	1.208	1.196

Mean value of $K=1.211$.*Allyl Bromoacetate.*

<i>t</i>	0.000	0.834	2.067	3.000	3.750
<i>C_t</i>	0.00	13.79	28.86	36.36	41.78
<i>K</i>	—	0.769	0.766	0.771	0.765

Mean value of $K=0.768$.*Ethyl β-Bromopropionate.*

<i>t</i>	0.000	5.250	21.500	24.000	27.500	29.500
<i>C_t</i>	0.00	3.94	12.20	13.50	15.35	16.78
<i>K</i>	—	0.0313	0.0258	0.0260	0.0264	0.0273

Mean value of $K=0.0277$.*Bromoacetal.*

<i>t</i>	0.000	18.000	21.000	26.000
<i>C_t</i>	0.00	5.21	6.02	6.87
<i>K</i>	—	0.0122	0.0122	0.0114

Mean value of $K=0.012$.*Chloroacetamide.*

<i>t</i>	0.000	19.170	21.167	23.500	45.333
<i>C_t</i>	0.00	5.09	5.78	6.14	11.22
<i>K</i>	—	0.01120	0.01155	0.01113	0.01070

Mean value of $K=0.01115$.*Chloroacetanilide.*

<i>t</i>	0.000	4.600	5.417	6.867	20.750	24.065
<i>C_t</i>	0.00	2.96	3.55	3.94	12.01	13.20
<i>K</i>	—	0.0265	0.0274	0.0258	0.0268	0.0263

Mean value of $K=0.0264$.

Bromoacetanilide.

<i>t</i>	0.000	1.000	1.500	1.934	2.834	3.283	3.483
<i>C_t</i>	0.00	27.65	36.50	41.85	52.80	56.35	57.60
<i>K</i>	—	1.463	1.532	1.485	1.578	1.673	1.565

 Mean value of *K* = 1.533.

Diphenylchloroacetamide.

<i>t</i>	0.000	10.500	12.000	14.000	15.500	18.500
<i>C_t</i>	0.00	8.20	9.40	10.60	11.80	13.40
<i>K</i>	—	0.0340	0.0346	0.0339	0.0345	0.0325

 Mean value of *K* = 0.0341.

Chloroacetone.

<i>t</i>	0.000	3.758	5.550	20.550	22.500	24.330
<i>C_t</i>	0.00	6.30	8.68	28.20	27.40	29.35
<i>K</i>	—	0.0715	0.0683	0.0691	0.0661	0.0682

 Mean value of *K* = 0.0686.

Chloroacetophenone.

<i>t</i>	0.000	5.100	11.550	15.500	16.333
<i>C_t</i>	0.00	14.56	27.75	34.30	35.45
<i>K</i>	—	0.1336	0.1330	0.1346	0.1345

 Mean value of *K* = 0.1339.

Bromoacetophenone.

<i>t</i>	0.000	0.333	0.500	0.667	0.833	1.000	1.333
<i>C_t</i>	0.00	37.65	48.00	54.91	60.30	63.75	71.02
<i>K</i>	—	7.252	7.382	7.301	7.288	7.035	7.358

 Mean value of *K* = 7.269.

The following two series of measurements were carried out in 25 per cent. aqueous alcohol (by volume); temperature 55.6°; initial concentration *N*/8:

Methyl Bromoacetate.

<i>t</i>	0.0000	0.1166	0.2000	0.2835	0.3667	0.4500	0.5333
<i>C_t</i>	0.00	17.60	27.20	34.40	40.00	44.80	48.80
<i>K</i>	—	14.65	14.95	14.81	14.54	14.43	14.30

 Mean value of *K* = 14.61.

Potassium Bromoacetate.

<i>t</i>	0.0000	0.2000	0.3667	0.5333	0.7000	0.8568	1.0333
<i>C_t</i>	0.00	18.40	29.60	37.60	44.00	49.60	53.60
<i>K</i>	—	9.02	9.13	9.06	8.98	9.10	9.09

 Mean value of *K* = 9.07.

The following compounds quoted in the foregoing list are not described in the literature.

Cinnamyl Bromide, $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{Br}$.—Cinnamyl alcohol was saturated with dry hydrogen bromide at the ordinary temperature, heated to 100° for two hours to decompose the resulting additive product, washed with dilute alkali and with water, dried, and distilled under diminished pressure. It is an almost colourless oil, boiling at $122\text{--}123^\circ/10$ mm., insoluble in water, and moderately soluble in organic solvents:

0.1830 gave 0.1752 AgBr. Br = 40.74.

$\text{C}_9\text{H}_9\text{Br}$ requires Br = 40.62 per cent.

n-Butyl Bromoacetate, $\text{CH}_3\text{Br}\cdot\text{CO}_2\cdot\text{C}_4\text{H}_9$.—Equimolecular quantities of bromoacetic acid and *n*-butyl alcohol with a few drops of concentrated sulphuric acid were heated to 100° for three hours, the product being washed with dilute alkali and with water, dried, and distilled under diminished pressure. The substance is a colourless liquid, boiling at $78^\circ/10$ mm., and is insoluble in water, but miscible with organic solvents; it possesses no sharp odour, thus differing from the other aliphatic esters examined:

0.1085 gave 0.1046 AgBr. Br = 41.02.

$\text{C}_6\text{H}_{11}\text{O}_2\text{Br}$ requires Br = 41.02 per cent.

tert.-Butyl Bromoacetate, $\text{CH}_3\text{Br}\cdot\text{CO}_2\cdot\text{CMe}_3$.—*tert.*-Butyl iodide was treated with a slight excess of dry silver bromoacetate suspended in ether, the mixture being kept cool. After twelve hours, the ethereal solution was filtered, and the ether distilled off, the residue being fractionated under diminished pressure. A yield of only about 20 per cent. was obtained of a colourless liquid, boiling at $50^\circ/10$ mm., insoluble in water, but miscible with organic solvents; it possesses a pungent odour, similar to that of methyl bromoacetate:

0.1747 gave 0.1691 AgBr. Br = 41.20.

$\text{C}_6\text{H}_{11}\text{O}_2\text{Br}$ requires Br = 41.02 per cent.

Benzyl Bromoacetate, $\text{CH}_2\text{Br}\cdot\text{CO}_2\cdot\text{CH}_2\text{Ph}$.—Benzyl alcohol and bromoacetic acid were esterified in the manner described under *n*-butyl bromoacetate. The ester is a colourless liquid boiling at $143^\circ/10$ mm., and insoluble in water, but miscible with organic solvents; it possesses an odour similar to that of benzyl acetate; the vapour does not attack the mucous membranes at the ordinary temperature:

0.2136 gave 0.1746 AgBr. Br = 34.82.

$\text{C}_9\text{H}_9\text{O}_2\text{Br}$ requires Br = 34.94 per cent.

Allyl Bromoacetate, $\text{CH}_2\text{Br}\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}=\text{CH}_2$.—Allyl alcohol and bromoacetic acid were esterified in the manner described under *n*-butyl bromoacetate. The ester is a colourless liquid, boiling at

73°/10 mm. It is insoluble in water, but miscible with organic solvents, and possesses an extremely sharp odour.
 0.1693 gave 0.1790 AgBr. Br=45.05.

$C_6H_7O_2Br$ requires Br=44.69 per cent.

Diphenylchloroacetamide, $CH_2Cl \cdot CO \cdot NPh_2$. — Diphenylamine, dissolved in dry carbon tetrachloride, was treated with excess of chloroacetyl chloride, the mixture being maintained at atmospheric temperature by immersion in cold water. The precipitated diphenylamine hydrochloride was separated, and the carbon tetrachloride removed from the filtrate by distillation. The residue, after being washed with water, was recrystallised from alcohol. The compound forms colourless needles, melting at 116°, and is moderately soluble in organic solvents:

0.1944 gave 0.1163 AgCl. Cl=14.80.

$C_{14}H_{12}ONCl$ requires Cl=14.45 per cent.

In conclusion, the author desires to express his thanks to Assistant-Professor Smiles and to Dr. A. W. Stewart for friendly interest and valuable advice.

CHEMICAL LABORATORY,
 UNIVERSITY COLLEGE, LONDON.

XLVII.—*The Vapour Pressures of Two Perfectly Miscible Solids and their Solid Solutions.*

By ERNEST VANSTONE, B.Sc. (Wales) (1851 Exhibition Research Scholar University College, Cardiff, formerly "Isaac Roberts" Research Scholar).

In a former paper (Trans., 1909, 95, 590) it was shown that camphor and hydroxycamphor or borneol form a continuous series of solid solutions. The vapour pressures of these substances and of their solid solutions have since been measured; the methods employed and results obtained form the subject of the present paper.

The Vapour Pressure of Camphor.

Measurements have previously been made by Ramsay and Young (Phil. Trans., 1884, Part I, 34) and by Allen (Trans., 1900, 77, 413). Ramsay and Young determined the vapour pressures for temperatures from 0° to 180°. The ordinary barometric method

was employed, and also a second method, in which the temperatures of volatilisation corresponding with different pressures were read on a thermometer the bulb of which was coated with a layer of camphor. This method gave good results for liquids, but does not seem satisfactory when used for solids. Concerning the barometric method, the authors state: "We think it right to give details as to the method of operation, as we found it a matter of extreme difficulty to expel all moisture and air." In spite of the precautions taken, I think it very probable that the results obtained were vitiated by the presence of a trace of air. The results obtained by the two methods are not very concordant, thus at 64° the barometric method gave 6.4 mm., whereas the second method gave 7.2 mm. at 48.9° .

Allen also used two methods, one being the barometric. He took the precaution to boil the mercury, but passed the camphor up in a small tube, and applied a correction for the air admitted.

The air-current method was also employed, the principle of which is to find the weight of camphor required to saturate a known volume of air. The saturation limit was, however, obtained by a method of extrapolation. Allen's work extended over temperatures from 0° to 80° . The vapour pressures measured were very small, the greatest being 9 mm. at 80° . There is considerable discrepancy between Allen's results and those of Ramsay and Young, thus at 48.9° the latter obtained 7.2 mm., whereas Allen at 50° obtained 1.3 mm. I therefore decided to make determinations by both the barometric and air-current methods for temperatures from 78° to 160° .

The Barometric Method.

The apparatus (Fig. 1) consisted of two tubes about 80 cm. long and 12 mm. internal diameter. One of these tubes was provided with a trap 20 cm. from the closed end. This tube served as a standard barometer, which was filled as follows:

Mercury was poured in until it extended a few cm. past the trap. The tube was then connected to the water pump, and the mercury boiled. After cooling, the tube was nearly filled with mercury, and heated to the boiling point of aniline in the vapour-jacket. By connecting to the pump and repeatedly tapping the tube, most of the air bubbles were removed. After cooling, the tube was completely filled and inverted in the trough. The second tube served as the experimental tube. A thick-walled capillary tube was sealed on one end, a piece of wider glass tubing a few mm. diameter next, and then the stopcock.

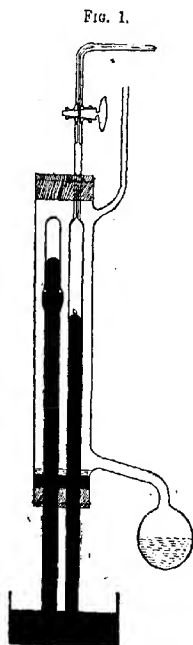
Both tubes were jacketed. The lower end of the jacket was closed by a doubly-bored rubber cork covered with a layer of

mercury, the upper end by an ordinary split cork. An experiment was conducted as follows. The experimental tube was connected to the pump by sealed glass joints, and the mercury pumped up. The tube was then heated to the boiling point of the liquid in the bulb, the pump kept at work, and the tube repeatedly tapped to remove bubbles from the side. It was then allowed to cool, and the camphor introduced as a small pellet under the mercury in the trough. The tube was again heated, and the pump worked. As the upper part of the tube became hot, the camphor vaporised, and some of it passed into the capillary portion, where it condensed and closed the tube.

When the vapour was condensing well up in the side-tube, the heights of the mercury in the barometer and experimental tube were read by means of a cathetometer, provided with a vernier which enabled readings to be made to 0.01 mm. The telescope of the cathetometer was brought into the horizontal by focussing on the surfaces of the mercury in the limbs of a wide U-tube clamped near the top of the apparatus. Readings were taken until the pressure was constant. The apparatus was then allowed to cool, and readings again taken at room temperature. If the difference in level was now greater than 0.1 mm., the capillary tube was gently heated; the camphor which had condensed there was by this means driven back into the experimental tube or into the upper wider portion, and thus the passage to the pump was again open. The above operations were then repeated until the desired result was obtained.

This made it certain that all the air and moisture had been removed, the vapour pressure of camphor at room temperature being about 0.1 mm. It was found more convenient to make observations at the highest temperature first, as on passing from a lower to a higher temperature air bubbles always appeared on the sides of the tube.

In the early experiments a Töpler pump was used, but later a



Fleuss pump was placed at my disposal, and the work became far less tedious. Accurate results at five temperatures were obtained, the temperatures being the boiling points of the following liquids under atmospheric pressure: ethyl alcohol, 78°; propyl alcohol, 96°; toluene, 110°; chlorobenzene, 130°; and bromobenzene, 156°.

The temperatures were read on Anschütz normal thermometers (which had been previously standardised) placed inside the jacket. These could be read to 0.1°. In some cases the temperatures were obtained by reading the barometer, from Ramsay and Young's table of vapour pressures.

The following results were obtained:

Vapour Pressure of Camphor.

Temperature.	Number of readings.	Vapour pressure.
78.0°	30	6.40 mm.
96.8	6	16.15 "
110.9	20	33.00 "
131.1	28	75.37 "
131.4	16	76.00 "
132.0	15	76.61 "
157.0	14	181.50 "

The Vapour Pressure of Borneol.

The vapour pressure of borneol has not been previously measured. It was determined in the same manner with the following results:

Temperature.	Number of readings.	Vapour pressure.
77.9°	6	2.16 mm.
96.8	11	6.65 "
110.0	9	14.94 "
131.0	16	40.92 "
156.0	14	115.16 "

The Air-Current Method.

The apparatus was the same as that used by Perman and Davie in finding the vapour pressures of naphthalene and dilute solutions of naphthalene and β -naphthol (Trans., 1907, 91, 1114). Details are given in that paper. A stopcock replaced the ground glass stopper, and a larger bulb was necessary for condensing the camphor. The stopcock was sealed on after introducing the camphor. A thermostat containing water and a toluene regulator were used for temperatures below 100°; for higher temperatures olive oil and a mercury regulator were employed. In order that the pressure of the air in the spiral should be the same before and after the experiment, it was placed in the thermostat and a current of air drawn through for some time; the stopcock was then closed, the spiral removed, the camphor washed out of the bulb with

alcohol and ether, the spiral cleaned by immersing in light petroleum, dried, and weighed. It was again placed in the thermostat, and a known volume of air drawn over, then cleaned and weighed as before.

The temperature of the aspirator and the height of the barometer were observed at the end of the experiment.

Method of Calculation.—If w = weight in grams of camphor withdrawn :

P = pressure of atmosphere in mm.

p = " air in aspirator in mm.

T = absolute temperature of aspirator.

V = volume of air aspirated, in litres.

v_c = specific volume of camphor vapour = $\frac{22.41}{M}$.

M = molecular weight of camphor.

then, assuming the truth of Dalton's Law of Partial Pressures, the following relationship holds good :

$$\frac{\text{Pressure of camphor vapour}}{\text{Total pressure.}} = \frac{\text{Volume of camphor vapour}}{\text{Total volume.}}$$

$$\frac{p_c}{P} = \frac{wv_c}{V + wv_c}$$

correcting volume V for temperature and pressure we get :

$$p_c = \frac{wv_c TP 760}{273 pV + 760 wv_c T}$$

The following results were obtained :

w .	P (mm.).	V .	p .	T .	Time (mins.).	t° .	p_c (mm.).
0.4169	752.2	7.305	728.7	288.9°	540	77.9	6.823
0.3439	765.0	5.915	752.6	287.5	370	78.0	6.904
0.2592	756.5	4.439	744.2	287.4	325	78.0	6.746
0.3456	763.6	5.915	751.6	287.1	480	78.0	6.923
0.3379	759.8	5.915	747.0	288.2	350	78.0	6.805
0.3355	764.9	5.915	752.2	287.9	330	77.9	6.750
0.2561	763.6	4.439	750.8	288.2	285	78.0	6.872
0.2555	759.9	4.439	746.3	289.0	555	78.0	6.800

Mean vapour pressure at 78° 6.828

0.3956	758.7	2.957	744.9	289.2	150	95.2	15.820
0.3994	759.0	2.957	745.3	289.1	180	95.1	15.961
0.3952	761.2	2.957	747.3	289.3	280	95.1	15.812
0.4016	763.2	2.957	749.1	289.6	250	95.2	15.983
0.3927	765.6	2.957	750.2	291.0	220	95.1	15.835
0.3960	766.1	2.957	750.4	291.3	240	95.1	15.989
0.4065	764.1	2.959	748.4	291.3	270	95.1	15.981
0.3908	766.5	2.959	761.7	290.4	255	95.1	15.711
0.3559	765.4	2.959	750.8	290.2	270	95.1	15.896

Mean vapour pressure at 95° 15.880

434 VANSTONE: THE VAPOUR PRESSURES OF TWO PERFECTLY

w .	P (mm.).	V .	p .	T .	Time (mins.)	t .	P (mm.).
0.3863	760.3	1.4764	746.4	289.3	80	109.0	30.266
0.3870	764.3	1.4764	750.8	288.8	80	109.0	30.247
0.3875	763.3	1.4764	749.7	289.0	80	109.2	30.410
0.3875	762.2	1.4764	748.4	289.2	80	109.0	30.435
Mean vapour pressure at 109°							30.390
1.3500	759.5	2.959	750.0	283.4	135	120.3	50.15
1.3332	762.0	2.959	752.3	288.9	150	120.2	49.67
1.3044	767.1	2.959	758.1	282.7	150	120.0	48.45
1.2940	751.0	2.959	741.8	284.0	180	120.0	48.30
Mean vapour pressure at 120°							48.37
1.0100	746.3	1.4764	736.1	284.6	115	130.4	73.04
1.0064	744.2	1.4764	734.1	284.4	70	130.4	72.73
1.0090	748.5	1.4764	738.7	283.9	70	130.4	72.72
Mean vapour pressure at 130.4°							72.84
0.6859	758.6	1.000	744.6	289.5	60	131.2	74.78
0.6892	759.1	1.000	745.1	289.4	35	131.3	75.09
0.6908	759.5	1.000	745.5	289.5	35	131.3	75.273
0.6928	757.7	1.000	743.4	289.7	40	131.5	75.528
Mean vapour pressure at 131.3°							75.17
1.0352	774.4	1.000	765.7	282.2	55	139.9	104.77
1.0248	773.9	1.000	764.8	282.9	60	139.9	104.12
1.0304	774.1	1.000	764.8	283.3	50	140.1	104.76
1.0204	774.2	1.000	765.6	282.0	50	139.6	103.40
Mean vapour pressure at 140°							104.5
1.5830	765.7	1.000	756.4	282.9	90	150.0	149.93
1.5872	764.0	1.000	754.6	283.3	60	150.0	150.03
1.6014	766.4	1.000	757.7	282.2	45	150.1	150.56
Mean vapour pressure at 150°							150.13
2.0410	758.5	1.000	744.3	298.8	60	156.0	186.48
2.0154	764.0	1.000	750.6	286.8	60	156.0	184.34
Mean vapour pressure at 156°							185.4

It is seen from the above that for temperatures of 120° and upwards, considerable quantities of camphor were drawn off. A larger spiral was used in these experiments. At 150° the camphor showed signs of charring. The rate at which the air was drawn over was varied widely to ensure saturation.

The results obtained by the two methods are compared in the following table:

Temperature.	Barometric (mm.).	Temperature.	Air current (mm.).
78.6°	7.09	78.1°	6.83
96.8	16.15	95.1	15.88
111.0	33.00	110.9	33.00
131.0	75.00	131.1	75.20
157.0	181.5	156.0	185.4

The agreement is very close; the high^a values given by the air-current method at 150° and 156° are probably due to charring of the camphor. The vapour pressures at the temperatures of Ramsay and Young's experiments and those of Allen have been obtained by graphic interpolation.

These are given in the table below:

Temperature.	Vapour pressure (mm.).	Ramsay and Young (mm.).	Allen (mm.).
78.4*	6.8	9.5 *	7.62
80.0	7.1	—	9.15
92.4	13.1	15.4 *	—
100.0	19.5	22.6	—
101.0	20.5	27.2	—
109.4	30.3	35.0	—
116.7	42.6	46.0	—
127.4	65.5	66.3	—
132.0	76.7	78.1	—
134.2	84.2	88.6	—
136.3	91.0	92.8	—
140.3	105.0	105.0	—
141.7	110.0	109.4	—
147.0	131.0	155.1	—
154.3	165.8	197.6	—

* These results were obtained by the barometric method.

It is seen that the present results are at nearly all temperatures lower than those of the other investigators.

The vapour pressures of borneol were also determined by the air-current method, with the following results:

w.	P.	V.	p (mm.).	T. (mins.).	t°.	V.P. (mm.).
0.005	753.7	5.021	742.8	285.7 ^a	390	78.0 2.213
0.1085	755.9	5.021	745.8	284.5	390	78.0 2.344
0.1072	758.8	5.021	749.3	283.6	345	78.1 2.358
Mean vapour pressure at 78°						2.305
0.2912	761.6	5.021	751.5	284.5	255	95.0 6.708
0.2353	758.1	5.021	747.7	284.9	270	95.1 6.597
0.2884	752.3	5.021	741.6	285.4	350	95.3 6.671
0.2908	763.9	5.021	753.2	285.4	300	95.3 6.725
Mean vapour pressure at 95.2°						6.675
0.4105	746.7	3.0024	736.8	285.7	180	110.5 15.765
0.4095	754.1	2.9545	743.2	285.7	180	110.5 15.920
0.3318	751.1	2.9180	740.2	285.7	180	109.8 15.450
0.3523	754.1	2.6185	742.9	286.0	180	110.4 15.508
0.2039	755.5	1.4825	744.3	286.1	180	110.9 15.829
0.2023	765.0	1.4825	752.0	286.8	85	110.4 15.685
Mean vapour pressure at 110.4°						15.72
0.3344	763.3	1.4825	752.1	286.0	60	120.0 25.666
0.3330	752.4	1.4825	741.6	285.5	60	120.0 25.463
0.3286	764.4	1.4825	764.1	284.8	60	120.0 25.465
Mean vapour pressure at 120°						25.371

436 VANSTONE: THE VAPOUR PRESSURES OF TWO PERFECTLY

w .	P .	V .	p (mm.)	T .	Time (mins.)	t .	$V.P.$ (mm.)
0.5470	765.9	1.4825	756.1	284.0	60	130.4	40.662
0.5397	767.3	1.4825	757.5	284.0	60	130.0	40.143
Mean vapour pressure at 130.2°.....							40.40
0.6016	770.6	1.00	760.7	284.2	45	139.9	61.181
0.5983	770.4	1.00	760.2	284.3	45	140.1	63.936
Mean vapour pressure at 140°							61.06
0.4738	769.9	0.500	759.8	284.5	45	150.2	96.521
0.4743	769.6	0.500	759.3	284.8	45	150.2	96.814
Mean vapour pressure at 150.2°.....							96.66
0.6910	768.4	0.500	757.9	285.1	30	159.2	133.31
0.6560	767.7	0.500	757.2	285.1	30	158.4	127.20

These results are compared below with those obtained by the barometric method:

Temperature.	Air current (mm.).	Temperature.	Barometric (mm.).
78.0°	2.30	77.9°	2.16
95.2	8.67	96.3	6.55
110.5	15.70	110.0	15.00
130.2	40.4	131.0	40.92
150.2	96.6	156.0	115.16
158.4	127.2	—	—

As in the case of camphor the results agree closely,

Ramsay and Young have shown that the ratio of the boiling points expressed as absolute temperatures of closely related liquids is constant. As the two solids investigated are also very closely related, the ratios of the absolute temperatures corresponding with equal vapour pressures have been calculated:

Pressure (mm.).	T_c .	T_B .	T_B/T_c .
10	360.3	376.0	1.043
20	373.5	388.4	1.040
30	381.8	396.4	1.038
40	388.3	403.0	1.038
50	393.3	407.8	1.037
60	398.0	411.6	1.034
70	401.3	415.0	1.034
80	405.9	418.0	1.030
90	409.0	421.2	1.030
100	411.8	423.7	1.029
110	415.3	426.3	1.026

The constancy of the ratios is evident.

The Vapour Pressures of Solid Solutions.

One of the chief difficulties of previous investigators has been to obtain solid solutions having vapour pressures large enough to be accurately measured. The only work of importance is that of Speransky (*Zeitsch. physikal. Chem.*, 1903, **46**, 70; 1905, **51**, 45).

who measured the vapour pressures of solid solutions of *p*-dichlorobenzene and *p*-dibromobenzene, and *p*-chlorobromobenzene and *p*-dibromobenzene. He concluded that "the regular laws which hold for liquid solutions also hold for solid solutions."

The Vapour Pressures of Solid Solutions by the Air-Current Method.

The equation given on page 433 for calculating the vapour pressure of camphor, when applied to solid solutions, becomes:

$$P_s = p_c + p_b = \frac{(w_c v_c + w_b v_b) P}{V + w_c v_c + w_b v_b} \quad (1)$$

where

P_s = vapour pressure of solid solution.

p_c and p_b = partial pressures of camphor and borneol.

w_c , w_b = weights in grams of camphor and borneol in the total weight (W) drawn off;

also

$$w_c + w_b = W \quad (2).$$

Equations (1) and (2) contain three unknowns, namely, w_c , w_b , and P_s , hence it seems impossible to determine the vapour pressure of a solid solution, in which both constituents have appreciable vapour pressures, by the air-current method alone. If, however, P_s can be obtained by the barometric method, w_c and w_b can be calculated, and p_c and p_b , the partial pressures of the constituents obtained.

Solving for w_c in this way, we get:

$$w_c = VP_s - Wv_b(P - P_s)/(v_c - v_b)(P - P_s).$$

It is obvious that this involves the difference between the specific volumes v_c and v_b , so that the method can only be applied to cases in which these differ fairly widely.

For camphor and borneol $v_c = 0.1473$ and $v_b = 0.1454$, hence the method is of no use in the present case; we may, however, write $v_c = v_b$ in equation (1), which then becomes:

$$P_s = \frac{Wv_c P}{V + Wv_c},$$

thus the total vapour pressure of a solid solution can be obtained approximately by the air-current method. The error involved is about 1.2 per cent.

A series of experiments was carried out at 110° . The difficulties were now very much greater, as change in concentration had to be avoided as far as possible.

The temperature of 110° was chosen for two reasons: (1) The weight of substance drawn off by aspirating a litre of air through

the spiral was small, and hence the change in concentration of the solution would be small; (2) the vapour pressure at that temperature was large enough to be accurately measured by the barometric method, that for camphor being 33 mm. and for borneol 15 mm.

The solutions were made by fusing the accurately weighed quantities of camphor and borneol in sealed tubes. These were then broken, the mass removed, cut up in small pieces, dried over sulphuric acid, and introduced into the dry spiral. The spiral was placed in the thermostat, and a few c.c. of air drawn through; the stopcock near the condensing bulb was then turned off, the other end of the spiral closed by means of a small india-rubber stopper, the spiral removed, cleaned, and weighed. It was then again placed in the thermostat, and a known volume of air drawn through, again closed, cleaned, and weighed. It was necessary to clean out the spiral after each experiment, and refill with a fresh quantity of solution.

The following results were obtained:

Mols. of borneol per 100 of mixture.	<i>W.</i>	<i>P.</i>	<i>p.</i>	<i>V.</i>	<i>T.</i>	Time (mins.).	<i>t.</i>	<i>p.</i> (mm.)
10	0.2632	769.8	765.5	1.00	288.8°	75	110.1	30.52
	0.2642	750.6	737.5	1.00	288.5	75	110.1	30.62
	0.2645	762.4	749.0	1.00	288.9	75	110.1	30.12
20	0.2404	771.1	758.5	1.00	287.9	90	110.1	27.31
	0.2406	770.7	757.7	1.00	288.3	75	110.1	27.90
30	0.2332	754.2	740.9	1.00	288.8	80	110.0	27.16
	0.2345	755.8	742.4	1.00	288.9	80	110.0	27.25
40	0.2144	747.1	734.7	1.00	287.6	90	110.1	25.21
	0.2154	760.9	747.2	1.00	289.2	110	110.1	24.36
50	0.2054	753.7	740.7	1.00	289.2	110	110.1	24.00
	0.2045	754.8	740.0	1.00	289.3	75	110.0	23.96
60	0.2642	763.5	750.3	1.4825	288.6	100	110.1	20.37
	0.2642	763.5	750.0	1.4825	289.0	150	110.1	20.38
70	0.2510	764.3	750.4	1.4825	294.4	100	110.0	19.33
	0.2510	764.8	750.7	1.4825	289.7	105	110.0	19.44
80	0.2280	765.3	751.9	1.4825	290.0	100	110.1	18.24
	0.2284	765.1	750.5	1.4825	290.2	100	110.1	18.17
90	0.2244	764.3	749.7	1.4825	290.2	90	110.1	17.99
	0.2232	763.8	749.1	1.4825	290.3	100	110.1	17.81
100	0.2662	758.7	744.1	1.00	290.2	90	110.0	15.00
	0.2682	758.7	744.1	1.00	290.2	100	110.0	15.10

Attempts were made to confirm these results by the barometric method. The difficulties were now even greater, and the results can only be regarded as approximate.

To remove air and moisture, to prevent any change in concentration by having a large quantity of substance present, and yet not so much as might obscure the mercury meniscus, was indeed extremely difficult. The experimental tube was now provided with a three-way tap in place of the ordinary stopcock previously used.

The junction of the tube nearest the capillary was well ground on the inside. This enabled the tube to be closed by a ground-glass stopper, sealed to a long glass rod, which passed down the tube beneath the mercury in the trough, being bent at its lower end so that it could be moved from the outside. One branch of the three-way tap communicated with the air pump, the other with a small reservoir of mercury.

The plan was to cause the substance to sublime quite near the top of the tube, keeping the pump at work, then to run in mercury on the top of the ground joint closed by the stopper, and so effectively close the tube.

Experiments with solutions containing 20, 40, 60, and 80 molecules of borneol per 100 molecules of mixture were made. For the experiments with the 20 per cent. solution, a three-way tap and a capillary tube alone were used, mercury being run into the capillary tube. There was some loss by sublimation into the portion outside the vapour jacket, whilst it is certain that air and moisture were removed.

Experiments were made with the same solution at five temperatures, as in the case of the pure substances.

The apparatus had to be taken down and the tube cleaned out before proceeding to make observations with a solution of different concentration, and often for the same solution as the quantity of substance necessary at the high temperatures obscured the mercury meniscus at the lower temperatures.

*Vapour Pressures of Solid Solutions of Camphor and Borneol.
Barometric Method.*

Molecules of borneol per 100 of mixture = 20.

Temperature.	Number of readings.	Vapour pressure.
78.6°	5	6.10 mm.
97.0	4	15.90 „
97.4	6	16.04 „
110.6	15	28.18 „
131.6	4	66.90 „
131.8	6	67.50 „
156.2	6	159.40 „

Molecular Concentration=40 per cent. borneol.

Temperature.	Number of readings.	Vapour pressure.
78.4°	5	5.54 mm.
97.2	5	13.27 "
110.0	5	25.60 "
131.0	5	63.70 "
156.4	5	150.5 "

Molecular Concentration=60 per cent. borneol.

Temperature.	Number of readings.	Vapour pressure.
78.5°	7	4.83 mm.
97.1	6	11.40 "
110.2	5	23.05 "
131.2	5	60.58 "
156.0	7	140.00 "

Molecular Concentration=80 per cent. borneol.

Temperature.	Number of readings.	Vapour pressure.
78.6°	6	3.56 mm.
96.8	4	8.80 "
97.1	5	9.10 "
110.6	4	19.70 "
110.8	4	20.00 "
131.8	4	56.40 "
156.2	10	130.20 "

These results, as well as those for camphor and borneol, have been plotted on a temperature-pressure diagram (Fig. 2); it is seen that the curves for the solutions lie between those for the pure substances. The vapour pressures obtained by both methods are compared in the following table:

Concentration.	Temperature.	Barometric (mm.).	Temperature.	Air current (mm.).
20 mols. borneol	110.6°	28.1	110.1°	27.8
40 " "	110.0	25.8	110.1	25.0
60 " "	110.2	23.0	110.8	20.8
80 " "	110.6	19.7	110.1	18.2

The deviations are in the direction expected, since the errors are entirely due to change in concentration. For those solutions relatively richer in camphor, the barometric method would give, owing to loss of the more volatile component, results which would be too low, and conversely for solutions relatively richer in borneol. The agreement is as close as can be expected, considering the extreme difficulty of determining the vapour pressure of a solid solution by the barometric method.

Isothermals are shown in Fig. 3. The results given at 110° are those obtained by the air-current method; for other temperatures the barometric results are given. It is seen that the isothermals

FIG. 2.

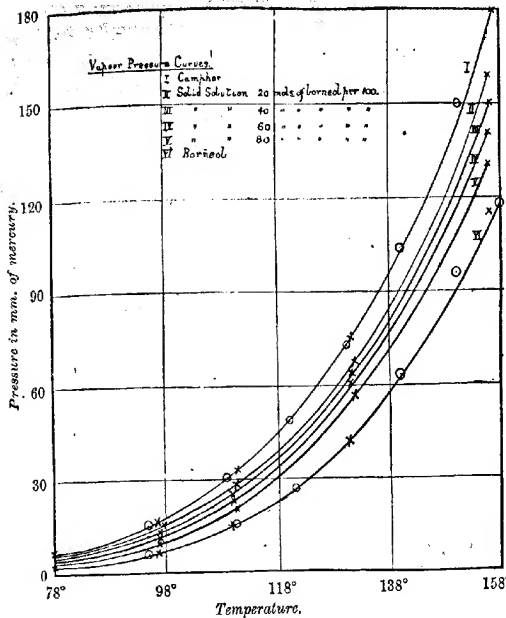
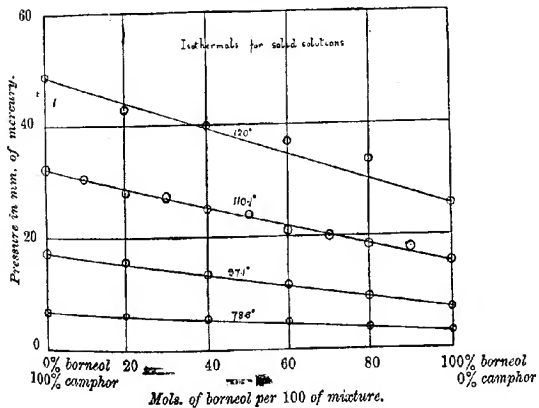


FIG. 3.



are straight lines. This leads to the important conclusion "that the vapour pressure of a solid solution is a linear function of the molecular concentration, and can be calculated from the equation:

$$P_s = \frac{nP_s + (100 - n)P_c}{100},$$

where n = number of mols. of borneol per 100 mols. of mixture.

The calculated and observed results are given in the following table:

Vapour Pressure of Solid Solutions at 110°.

Concentration.	Calculated.	Observed (air-current method).
10	30.3 mm.	30.4 mm.
20	28.6 "	27.8 "
30	26.9 "	27.1 "
40	25.2 "	25.0 "
50	23.5 "	24.0 "
60	21.8 "	20.9 "
70	20.1 "	19.9 "
80	18.4 "	18.2 "
90	16.7 "	17.9 "

Speransky (*ibid.*), for solid solutions of *p*-chlorobromobenzene and *p*-dibromobenzene, obtained fairly good agreement between calculated and observed vapour pressures. The pressures were measured in mm. of paraffin oil in a differential tensimeter. Young (Trans., 1902, **81**, 768) has shown that the equation given above holds for mixtures of liquids which are chemically closely related, hence the present work is strong evidence in support of the van't Hoff theory of solid solutions, that they follow the same laws as liquid solutions. It is seen also from the curves in Fig. 2 that the vapour pressures of solid solutions of camphor and borneol are always greater than the vapour pressure of borneol. Precisely the same may be said of the freezing points, hence, when the substance of lower freezing point and vapour pressure is considered, the addition of a substance with which it forms solid solutions produces a change in these properties opposite to that expected, and directly contrary to that which usually occurs with solutions which obey Raoult's law. It seems therefore futile to apply such laws to determine the molecular weight of solids.

Summary and Conclusion.

1. The vapour pressures of camphor and borneol have been determined for temperatures from 78° to 156°. The results, obtained for camphor are generally lower than those of former investigators. The vapour pressure of borneol has not been previously determined.

2. The ratio of the absolute temperatures corresponding with

equal vapour pressures is constant, thus Ramsay and Young's rule for closely related liquids also holds for closely related solids.

3. The air-current method of determining vapour pressures has been extensively used, and it has been shown that the results obtained agree closely with those obtained by the barometric method.

4. The vapour pressures of a complete series of solid solutions have been determined. It has been shown that the vapour pressures of solid solutions, like other physical properties, follow the ordinary mixture law:

$$p_s = \frac{np_A + (100 - n)p_B}{100},$$

where n = number of mols. of A per 100 of mixture.

5. Approximate results for solid solutions have been obtained by the barometric method, more accurate results by the air-current method.

6. A method of determining the partial pressures of solutions by combining the data obtained from barometric and air-current methods has been indicated.

7. Since the vapour pressures of solid solutions of camphor and borneol follow the mixture law, it is highly probable that the molecular weights of the solid components are normal.

8. The agreement between the results obtained by the two methods leads to the conclusion that the densities of the vapours of camphor and borneol at the temperatures employed are normal.

In conclusion, I wish to express my thanks to the Principal of University College, Cardiff, and the staff of the chemical department, for the interest taken in the work and the facilities afforded me. I am especially grateful to Dr. E. P. Perman for suggesting the work, and for his advice and assistance in carrying it out. The expenses of the work have been defrayed by grants from the Glamorgan County Council and the College Council, to whom also I wish to express my thanks.

UNIVERSITY COLLEGE,
LONDON, W.C.

XLVIII.—*Salts and Ethers of 2:3:5-Trinitro-4-acetylaminophenol.*

By RAPHAEL MELDOLA, F.R.S., and HAROLD KUNTZEN.

THE marked acid character of the above compound, which was first described by one of the authors in 1906 (*Trans.*, **89**, 1935), is shown by the readiness with which it forms metallic and organic salts. At the same time, the extreme mobility of one of the nitro-groups tends to bring about decomposition of the salts, especially in presence of excess of base. With organic bases of the nature of primary amines, the trinitro-compound, as stated in former papers, readily forms salts, but these pass rapidly into catenation products and finally into iminazoles, so that the intermediate product generally consists of a mixture of the salts of the trinitro-compound with those of the catenation product, or of the iminazole, or of both. With respect to metallic salts, it was pointed out in a recent communication (*Trans.*, 1909, **95**, 1381) that these could be safely prepared by the interaction of the trinitro-compound and salts of metals with weak acids. This principle has now been successfully applied for the preparation of a number of metallic and organic salts from the acetates, carbonates, etc., of the respective metals or alkaloids. Details of the mode of preparation of the various salts are given in the experimental part of this paper, the series described comprising those which are sufficiently insoluble in water to crystallise from the hot concentrated solution on cooling. This series is, however, quite typical, and the research has not been extended to those more soluble salts (lithium, calcium, etc.) which could not be directly isolated in the manner described, but which could no doubt be obtained if wanted by the evaporation of their solutions in a vacuum at the ordinary temperature.

General Characters of the Salts.

The metallic salts of trinitroacetylaminophenol are all highly coloured, red substances, the parent compound being pale yellow.* It is for this, among other reasons, that these salts have been considered of sufficient interest to form the subject of a special study in view of the large amount of work which has of late years been bestowed upon the subject of colour in relation to chemical constitution. It has already been pointed out that the trinitro-compound is capable of a double "isonitro-" isomerism (*Trans.*,

* The lead salt alone approaches the free trinitro-compound in colour.

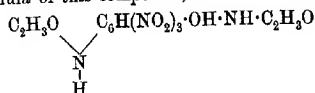
1908, 93, 1662), so that a change in constitution in passing from the free compound to the salt might reasonably be postulated. As satisfactory evidence of such change was most likely to be furnished by a study of the absorption spectra, and as Dr. J. T. Hewitt has recently been dealing with this subject (Trans., 1909, 95, 1755), he has, at our request, been good enough to photograph the absorption spectra of the free compound and its salts, and his observations are appended to the present paper. As will be seen from these results, there is justification for the belief that in forming a salt the isonitro-constitution is acquired, and he has further obtained evidence of the transitory existence of a disodium salt in presence of excess of alkali. In connexion with these results, it is of interest to note that the methyl ether described in this paper (2:3:5-trinitro-4-acetylaminoanisole) is, to the eye, a colourless substance, and therefore may be presumed to have the same constitution as the free trinitro-compound.

All the metallic salts of trinitroacetylamino-phenol now made known are very soluble in water. They are beautifully crystalline, and contain water of crystallisation which in most cases cannot be expelled at 100°, and at higher temperatures decomposition takes place. They all deflagrate on heating in the dry state, but not explosively, the only exception being the cobalt salt, which deflagrates more sharply than any of the others.

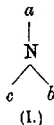
In forming salts with natural alkaloids, the trinitro-compound shows marked preferential characters. With brucine and guanidine very stable insoluble salts separate at once on mixing solutions of the trinitro-compound and the base, or by the action of the trinitro-compound on the acetate of the base. Narcotine forms a less stable salt, whilst carbamide, theobromine, quinine, strychnine, cinchonine, and morphine do not give readily isolable salts. Caffeine forms a salt which is interesting as being dissociable in alcoholic solution. If equimolecular weights of the base and the trinitro-compound are dissolved in a small quantity of boiling alcohol, the solution, on cooling, deposits at first crystals of caffeine, and subsequently a mixture of caffeine and the caffeine salt, the latter crystallising in yellow, nodular aggregates. Further crystallisation of the mixed crystals leads to the same result, even when excess of trinitro-compound is intentionally added, so that the pure caffeine salt could not be isolated. In alcoholic solution there appears to be an equilibrium mixture, varying in composition with temperature and concentration, of free caffeine, free trinitro-compound, and caffeine salt.

Attempt to Prepare an Optically Active Compound Containing an Asymmetric Tervalent Nitrogen Atom.

The main object in studying the salts formed by the trinitro-compound with natural alkaloids was to test a somewhat plausible hypothesis which had suggested itself with respect to the possible asymmetry of the nitrogen atom in the trinitro-compound itself. From the formula of this compound,



it will be seen that the nitrogen atom is combined with two acid radicles (acetyl and the substituted trinitro-phenol residue) and one positive atom (hydrogen). In most of the attempts that have hitherto been made to resolve tervalent nitrogen compounds, the nitrogen atom has been combined with positive radicles, and the molecule as a whole has been basic in character.* The negative results have in these cases been attributed to *racemisation* due to hydrolytic dissociation of the salt or to the temporary assumption of quinquevalent function by the nitrogen atom. The trinitro-compound under investigation is certainly free from the latter objection, as it is strongly acid in character, and does not form salts with acids. On the other hand, disregarding for the present the possibility of hydrolytic dissociation, if there is any weight attaching to the hypothesis of mutual attractions and repulsions between the radicles in a molecule, it might be considered that three positive radicles attached to a nitrogen atom would by mutual repulsion favour the configuration sometimes assigned to such compounds (No. I), the "bonds" being in one plane:



When two strongly acid radicles and one positive atom are present it seemed, on this view, that every chance for displacement of the "bonds" would be given, and the asymmetric configuration (No. II) assumed. At any rate, the hypothesis seemed sufficiently plausible to be worth submitting to the test of experiment. The result, as

* By way of exception to this general statement, the attempt by Jones and Millington to resolve methylethylanilinesulphonic acid may be referred to (*Proc. Camb. Phil. Soc.*, 1904, 12, 489). In this case, also, the result was negative.

in former cases, was, however, negative. A specimen of the brucine salt was prepared by precipitating the trinitro-compound in alcoholic solution with a semi-molecular proportion of the base. The trinitro-compound recovered from the filtrate and from the salt by decomposition by acid was examined for us by Dr. T. Martin Lowry, but in neither specimen was there any trace of optical activity. Dr. Lowry reports that he made his observations with the acetone solution of the compound (4 grams per 100 c.c. in 2-dcm. tubes) by means of red (lithium) light. We desire to take this opportunity of expressing our thanks to Dr. Lowry for the assistance thus rendered.

Although the result is in this case negative, we propose continuing the investigation, as there still remains the possibility that the asymmetry may exist only while the trinitro-compound and the base are in combination.* To test this point, it will be necessary to prepare some salt more soluble than the brucine salt, and to compare its optical activity in some non-hydrolysing solvent with that of the base with which the trinitro-compound is combined.

EXPERIMENTAL

Ammonium Salt, $C_8H_5O_3N_4 \cdot NH_3$.

Prepared by dissolving the trinitro-compound in a hot concentrated solution of ammonium acetate and allowing to crystallise. Bright red, spherical aggregates of slender needles. The salt is anhydrous, and undergoes decomposition at about 203° when heated in a capillary tube:

0.0434 gave 8.6 c.c. N_2 (moist) at 12° and 761.3. $N = 23.56$.

$C_8H_5O_3N_5$ requires $N = 23.10$ per cent.

Sodium Salt, $C_8H_5O_3N_4Na \cdot 3H_2O$.

Prepared by dissolving the trinitro-compound in a hot concentrated solution of sodium carbonate. The salt separates slowly on cooling in long, transparent, ruby-red prisms. Professor W. J. Pope, who has been good enough to examine these crystals for us, reports that they "probably belong to the anorthic system. The acute bisectrix of a large axial angle emerges through the small end faces; the optic axial dispersion is marked, and the angle for blue is larger than that for red light":

0.1336 gave 17.55 c.c. N_2 (moist) at 12.2° and 747 mm. $N = 15.31$.

0.1132 „ 0.0220 Na_2SO_4 . $Na = 6.31$.

$C_8H_5O_3N_4Na \cdot 3H_2O$ requires $N = 15.47$; $Na = 6.36$ per cent.

* As bearing on this point, see a paper by Pope and Harvey (Trans., 1901, 79, 837).

On heating in the water-oven, the salt becomes opaque and brick-red in colour, and loses weight owing to dehydration and (possibly) partial decomposition, the loss of weight being somewhat in excess of that required by the $3\text{H}_2\text{O}$ indicated by the above analyses:

0.5486, heated in the water-oven, lost $0.0930 = 16.95$ per cent.

0.0506 (dried as above) gave 7.75 c.c. N_2 (moist) at 12° and 750.1 mm. $\text{N} = 18.01$.

0.1036 (dried as above) gave $0.0238 \text{Na}_2\text{SO}_4$. $\text{Na} = 7.45$.

$\text{C}_8\text{H}_5\text{O}_8\text{N}_4\text{Na}$ requires $\text{N} = 18.19$; $\text{Na} = 7.48$ per cent. A loss of $3\text{H}_2\text{O}$ requires 14.9, and of $3\frac{1}{2}\text{H}_2\text{O}$ 17.43 per cent.

Potassium Salt, $\text{C}_8\text{H}_5\text{O}_8\text{N}_4\text{K}$.

This salt has already been described (Trans., 1909, 95, 1381). To the former description we are now enabled to add that an anhydrous salt is formed on long exposure to the air at the ordinary temperature:

0.0678 gave 10.2 c.c. N_2 (moist) at 17° and 755.5 mm. $\text{N} = 17.31$.

0.0928 „ 0.0244 K_2SO_4 . $\text{K} = 11.81$.

$\text{C}_8\text{H}_5\text{O}_8\text{N}_4\text{K}$ requires $\text{N} = 17.28$; $\text{K} = 12.07$ per cent.

Barium Salt, $(\text{C}_8\text{H}_5\text{O}_8\text{N}_4)_2\text{Ba}, 3\text{H}_2\text{O}$.

This salt was prepared by two methods, first by dissolving the trinitro-compound in a hot solution of barium acetate, and secondly, by boiling the trinitro-compound with barium carbonate and water and filtering from excess of barium carbonate. In both cases the solution deposits the salt on cooling as flat needles of a deep red colour and having a slight metallic reflex in the mother liquor when viewed at an angle. The analyses of the specimens prepared by the barium acetate method were somewhat irregular, and indicate that a more definite salt is given by the other method:

0.0550 gave 7.15 c.c. N_2 (moist) at 19° and 758.5 mm. $\text{N} = 14.9$.

0.1099 „ 13.9 c.c. N_2 (moist) at 11.5° and 754.1 mm. $\text{N} = 14.92$.

0.0770 „ 0.0238 BaSO_4 . $\text{Ba} = 18.19$.

$\text{C}_{16}\text{H}_{10}\text{O}_{16}\text{N}_8\text{Ba}, 3\text{H}_2\text{O}$ requires $\text{N} = 14.71$; $\text{Ba} = 18.0$ per cent.

The salt does not lose weight on drying at 100° .

Magnesium Salt, $(\text{C}_8\text{H}_5\text{O}_8\text{N}_4)_2\text{Mg}, 6\text{H}_2\text{O}$.

Prepared as above from the trinitro-compound and magnesium acetate. Bright red prisms. The specimen analysed was twice crystallised from water:

0.1292 gave 17.85 c.c. N_2 (moist) at 18.5° and 753.4 mm. $\text{N} = 15.78$.

0.1122 gave 0.0161 $\text{Mg}_2\text{P}_2\text{O}_7$. $\text{Mg} = 3.24$.
 $\text{C}_{16}\text{H}_{10}\text{O}_{16}\text{N}_8\text{Mg}_2\cdot 6\text{H}_2\text{O}$ requires $\text{N} = 15.95$; $\text{Mg} = 3.03$ per cent.
 The salt does not lose water at 100° .

Zinc Salt, $(\text{C}_8\text{H}_5\text{O}_8\text{N}_4)_2\text{Zn}\cdot 6\text{H}_2\text{O}$.

Prepared as above from the trinitro-compound and zinc acetate.
 Bright red prisms, resembling the magnesium salt:

0.1633 gave 21.1 c.c. N_2 (moist) at 18° and 760 mm. $\text{N} = 14.92$.
 0.3240 „ 0.0352 ZnO . $\text{Zn} = 8.73$.
 $\text{C}_{16}\text{H}_{10}\text{O}_{16}\text{N}_8\text{Zn}\cdot 6\text{H}_2\text{O}$ requires $\text{N} = 15.05$; $\text{Zn} = 8.8$ per cent.
 The salt does not lose weight at 100° .

Cadmium Salt, $(\text{C}_8\text{H}_5\text{O}_8\text{N}_4)_2\text{Cd}\cdot 6\text{H}_2\text{O}$.

Prepared by boiling the trinitro-compound with water and cadmium carbonate, filtering from excess of carbonate, and allowing to cool, when the salt crystallises out in red scales:

0.1422 gave 16.9 c.c. N_2 (moist) at 13° and 765.3 mm. $\text{N} = 14.15$.
 0.1602 „ 0.0262 CdO . $\text{Cd} = 14.32$.
 $\text{C}_{16}\text{H}_{10}\text{O}_{16}\text{N}_8\text{Cd}\cdot 6\text{H}_2\text{O}$ requires $\text{N} = 14.17$; $\text{Cd} = 14.22$ per cent.

The salt darkens in colour and shows signs of fusion and decomposition when heated in the water-oven.

Nickel Salt, $(\text{C}_8\text{H}_5\text{O}_8\text{N}_4)_2\text{Ni}\cdot 4\text{H}_2\text{O}$.

Prepared as above from the trinitro-compound and nickel carbonate. The salt separates as dark brick-red prisms:

0.160 gave 22.3 c.c. N_2 (moist) at 14° and 745.8 mm. $\text{N} = 16.08$.
 0.2460 „ 0.0260 NiO . $\text{Ni} = 8.31$.
 $\text{C}_{16}\text{H}_{10}\text{O}_{16}\text{N}_8\text{Ni}\cdot 4\text{H}_2\text{O}$ requires $\text{N} = 15.99$; $\text{Ni} = 8.37$ per cent.

The salt undergoes no change at 100° . It deflagrates somewhat sharply when heated in the dry state.

Cobalt Salt, $(\text{C}_8\text{H}_5\text{O}_8\text{N}_4)_2\text{Co}\cdot 6\text{H}_2\text{O}$.

Prepared as above from the trinitro-compound and cobalt carbonate. Crystallises in bright red prisms:

0.1899 gave 24.2 N_2 (moist) at 11° and 764.3 mm. $\text{N} = 15.24$.
 0.1714 „ 0.0135 Co . $\text{Co} = 7.88$ per cent.
 $\text{C}_{16}\text{H}_{10}\text{O}_{16}\text{N}_8\text{Co}\cdot 6\text{H}_2\text{O}$ requires $\text{N} = 15.2$; $\text{Co} = 8.1$ per cent.

This salt differs from the nickel salt, not only in the quantity of water of crystallisation with which it combines, but also in the readiness with which it parts with this water. When heated in the water-oven, the salt becomes of a dark brick-red colour, and

loses practically all its water. The anhydrous salt becomes hydrated, and changes to a bright red colour on moistening with water:

0.5032, dried in water-oven, lost 0.071. $H_2O = 14.11$.

$C_{16}H_{10}O_{16}N_8Co, 6H_2O$ requires $H_2O = 14.66$ per cent.

0.0529 (dried as above) gave 7.85 c.c. N_2 (moist) at 9° and 749.6 mm. $N = 17.6$.

0.0446 (dried as above) gave 0.0042 Co. $Co = 9.44$.

$C_{16}H_{10}O_{16}N_8Co$ requires $N = 17.82$; $Co = 9.38$ per cent.

This salt, on heating, deflagrates more sharply than the nickel salt.

Manganese Salt, $(C_8H_5O_8N_4)_2Mn, 4H_2O$.

Prepared as before from the trinitro-compound and manganese carbonate. Dull red, rhombohedral prisms:

0.2152 gave 29.2 c.c. N_2 (moist) at 12.3° and 749.9 mm. $N = 15.9$.

0.1266 „ 0.0132 Mn_2O_3 . $Mn = 7.51$.

$C_{16}H_{10}O_{16}N_8Mn, 4H_2O$ requires $N = 16.08$; $Mn = 7.89$ per cent.

The salt darkens and shows signs of fusion and decomposition when heated in the water-oven.

Copper Salt, $(C_8H_5O_8N_4)_2Cu, 4H_2O$.

Prepared from the trinitro-compound and copper carbonate as before. Dull brick-red, transparent, rhombohedral prisms:

0.1273 gave 17.1 c.c. N_2 (moist) at 12° and 745.1 mm. $N = 15.63$.

0.1709 „ 0.0190 CuO . $Cu = 8.89$.

$C_{16}H_{10}O_{16}N_8Cu, 4H_2O$ requires $N = 15.88$; $Cu = 9.0$ per cent.

The salt becomes light brown and opaque on heating in the water-oven, and partly loses its water. Complete dehydration could not be effected without decomposition:

0.5247 lost 0.0528. $H_2O = 10.06$.

$C_{16}H_{10}O_{16}N_8Cu, 4H_2O$ requires $H_2O = 12$ per cent.

The salt thus dried gave the following results on analysis:

0.0874 gave 13.1 c.c. N_2 (moist) at 12° and 755 mm. $N = 17.68$.

0.0844 „ 0.0104 CuO . $Cu = 9.84$.

$C_{16}H_{10}O_{16}N_8Cu$ requires $N = 17.69$; $Cu = 10.03$ per cent.

Lead Salt, $(C_8H_5O_8N_4)_2Pb, 3H_2O$.

Prepared from lead carbonate and the trinitro-compound as above. Flat, orange needles:

0.0948 gave 7.5 c.c. N_2 (moist) at 14° and 752.2 mm. $N=13.36$.

0.1428 „ 0.0625 $PbSO_4$. $Pb=25.15$.

$C_{10}H_{10}O_8N_4Pb \cdot 3H_2O$ requires $N=13.48$; $Pb=24.83$ per cent.

This salt does not lose water at 100°.

Thallium Salt, $C_8H_5O_8N_4Tl$.

From the trinitro-compound and thallium carbonate by the same method. Brick-red, fern-like leaflets:

0.0779 gave 7.6 c.c. N_2 (moist) at 7.7° and 741.4 mm. $N=11.52$.

0.1577 „ 0.0770 $TlCl$. $Tl=41.60$.

$C_8H_5O_8N_4Tl$ requires $N=11.46$; $Tl=41.72$ per cent.

The salt undergoes no change at 100°.

Silver Salt, $C_8H_5O_8N_4Ag \cdot 3H_2O$.

The salt was prepared from the trinitro-compound and silver carbonate by the method described above. It generally crystallises in red prisms, but sometimes separates as orange-red scales. The analysis of the salt offered considerable difficulty, as the free trinitro-compound appears to interfere with the precipitation of the silver chloride. Good results were only obtained when the organic matter was destroyed by heating the salt in a sealed tube with fuming nitric acid for three hours at 190°. The water could not be completely expelled by heating in the water-oven; at this temperature the salt darkens, and, on long heating, shows signs of decomposition. About 102° the salt deflagrates:

0.0622 (air dried) gave 6.8 c.c. N_2 (moist) at 14° and 744.2 mm.

$N=12.59$.

0.2996 (air dried) gave 31 c.c. N_2 (moist) at 12° and 768 mm.

$N=12.38$.

0.2570 gave 0.0820 $AgCl$. $Ag=24.02$.

$C_8H_5O_8N_4Ag \cdot 3H_2O$ requires $N=12.53$; $Ag=24.14$ per cent.

A specimen dried in the water-oven gave the following results:

0.0682 gave 8.2 c.c. N_2 (moist) at 14° and 730.5 mm. $N=13.58$.

0.0564 „ 0.0201 $AgCl$. $Ag=26.82$.

$C_8H_5O_8N_4Ag$ requires $N=14.26$; $Ag=27.46$ per cent.

The salt is not only readily soluble in water, but also in methyl and ethyl alcohols, and by its means the methyl ether has been prepared, and is described in the present paper.

Brucine Salt, $C_8H_5O_8N_4 \cdot C_{28}H_{26}O_4N_2$.

This salt was prepared by adding to a hot saturated solution of the alkaloid in absolute alcohol an equimolecular proportion of the

trinitro-compound dissolved in the same solvent. It was also obtained by dissolving the trinitro-compound in a hot aqueous solution of brucine acetate and allowing to cool. In both cases the same salt is obtained. It is practically insoluble in alcohol, so that the trinitro-compound might be used as a precipitant for the base. It can be best purified by dissolving in hot glacial acetic acid, which does not appear to decompose the salt, diluting the solution with water, and allowing to crystallise. It separates, on cooling, in rosettes of deep reddish-brown needles, which appear ruby-red by transmitted light. The salt melts with decomposition at $222-224^{\circ}$:

0.2180 gave 0.4366 CO_2 and 0.0906 H_2O . $\text{C}=54.62$; $\text{H}=4.89$.

0.1322 „ 0.2648 CO_2 „ 0.0572 H_2O . $\text{C}=54.62$; $\text{H}=4.80$.

0.1268 „ 13.7 c.c. N_2 (moist) at 21° and 757.5 mm. $\text{N}=12.26$.

$\text{C}_{31}\text{H}_{32}\text{O}_{12}\text{N}_6$ requires $\text{C}=54.68$; $\text{H}=4.74$; $\text{N}=12.36$ per cent.

In connexion with this salt it is of interest to note that brucine also forms a very insoluble picrate.

Guanidine Salt, $\text{C}_8\text{H}_6\text{O}_8\text{N}_4\text{CH}_5\text{N}_3$.

This salt was prepared by dissolving guanidine carbonate in dilute acetic acid and saturating the hot solution with the trinitro-compound, the latter being added in small portions in the solid state. The salt crystallises out on cooling in dark brown needles, appearing ruby-red by transmitted light, and having a bronzy lustre when seen by reflected light. Purification was effected by crystallisation from hot water, in which the salt dissolves with an orange colour:

0.1781 gave 44.55 c.c. N_2 (moist) at 20.5° and 754.1 mm. $\text{N}=28.32$.

0.2170 „ 0.2502 CO_2 and 0.0650 H_2O . $\text{C}=31.44$; $\text{H}=3.32$.

$\text{C}_9\text{H}_{11}\text{O}_8\text{N}_7$ requires $\text{C}=31.29$; $\text{H}=3.21$; $\text{N}=28.41$ per cent.

The salt is quite stable; the melting point is 227° , and no loss of weight takes place at 100° .

Narcotine Salt, $\text{C}_8\text{H}_6\text{O}_8\text{N}_4\text{C}_{22}\text{H}_{22}\text{O}_7\text{N}$.

This salt was prepared from the trinitro-compound and the acetate of the base, or by mixing alcoholic solutions of the components in the usual way. Some difficulty was experienced in obtaining a pure product owing to the tendency of the salt to dissociate when crystallised from alcohol. The most satisfactory results on analysis were given by specimens crystallised from alcohol in the presence of a slight excess of the base:

0.0988 gave 0.1860 CO_2 and 0.0378 H_2O . $\text{C}=51.34$; $\text{H}=4.35$.

0.1348 „ 0.2552 CO_2 „ 0.0504 H_2O . $\text{C}=51.63$; $\text{H}=4.16$.

0.0355 gave 3.1 c.c. N_2 (moist) at 12° and 761.3 mm. $N = 10.30$.

$C_{12}H_{10}O_8N_4$ requires $C = 51.48$; $H = 4.19$; $N = 10.02$ per cent.

The salt crystallises in flat, yellow needles, melting at $193-194^\circ$.

Caffeine Salt, $C_8H_8O_8N_4 \cdot C_8H_{10}O_2N_4$.

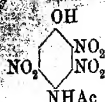
Although, for reasons stated in the introductory portion of this paper, the pure salt could not be isolated, the analytical results all pointed to the above formula. The salt, freed as far as possible from admixed caffeine, crystallises in rosettes of yellow needles, melting at about 177° .

Dr. J. T. Hewitt's Observations on the Absorption Spectrum of Trinitroacetylaminophenol and its Salts.

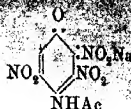
The pale yellow trinitro-compound dissolves both in water and 96 per cent. alcohol, with an intense yellow colour, inclining to orange. Whilst this orange shade is deepened by the addition of dilute sodium hydroxide or sodium acetate, the colour in the latter case soon reaching a maximum, hydrogen chloride has an opposite effect, comparatively small quantities causing the solution to assume a pale yellow tint comparable with that of the solid compound. This result is quite in accordance with the fact that trinitroacetylaminophenol is a fairly strong acid, and necessitates the addition of a highly ionised acid, such as hydrogen chloride, to the alcoholic solution if the spectrum of the non-ionised nitrophenol is to be observed (compare Buttle and Hewitt, *Trans.*, 1909, **95**, 1755, *et seq.*). In these circumstances the principal feature of the absorption spectrum was a band having its head at an oscillation frequency of about 2800, and not differing very markedly in this respect or in its persistency from that observed by Hartley and Huntington in the case of *o*-nitrophenol (see the curves plotted on a logarithmic scale by Baly, Edwards, and Stewart, *Trans.*, 1906, **89**, 519).

When an alcoholic solution to which a dilute alcoholic solution of sodium acetate has been added until no further intensification of the orange shade is noticeable (solution of the monosodium salt), a spectrum is obtained which in one respect shows a marked similarity to that observed by Baly and his co-workers (*loc. cit.*) in the case of the sodium salt of *o*-nitrophenol, and by Buttle and Hewitt (*loc. cit.*, p. 1756) with that of 2:6-dinitrophenol, the band of slowest vibration having its head at an oscillation frequency of 2250. Hence it seems justifiable to conclude that, as in the case of *o*-nitro- and 2:6-dinitro-phenols, formation of the sodium salt is accompanied by an alteration in structure, the trinitroacetylami-

phenol and its sodium salt, corresponding to the formula:



and



On the physical side there seems but little doubt that a radical alteration in absorption on formation of a derivative is accompanied by a radical alteration in structure, although it is well to keep in mind that the only direct *chemical* evidence bearing on the assumed change of structure on salt formation (or ionisation) in the case of the nitrophenols depends on the isolation of highly coloured acetates by Hantzsch and Gorke (*Ber.*, 1906, **39**, 1073).

If to a solution (aqueous or alcoholic) of the trinitro-compound, alkali be added in excess, a deep purple-red colour is produced; such solutions are, however, unstable, the decomposition making itself manifest by a deposition of sodium salt (? nitrite) when a solution in 96 per cent. alcohol is examined, and a change of colour towards yellow. Despite this inconvenience, an attempt was made to photograph the absorption spectrum of a freshly prepared solution, which very possibly contains a disodium salt: the persistency of the colour band was very similar to that found for a monosodium salt, but the head lies at an oscillation frequency of about 2040.

The curves in the figure were obtained with solutions made up in the following manner.

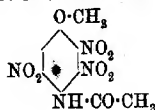
Trinitroacetaminophen (full curve).—A *N*/1000-solution was prepared from 0.0286 gram and 5 c.c. of fuming hydrochloric acid, made up to 100 c.c. with 96 per cent. alcohol. A *N*/10,000-solution was prepared by diluting 10 c.c. of the *N*/1000-solution and 5 c.c. of fuming hydrochloric acid to 100 c.c. with 96 per cent. alcohol.

Monosodium Salt (dotted curve).—0.0286 Gram of the phenol was dissolved in alcohol, a solution of sodium acetate added in at least twice the excess of that necessary to produce any further intensification of the orange shade, and then made up to 100 c.c. with alcohol. 5 mm. of this *N*/1000-solution gave the same absorption as 50 mm. of the solution obtained on tenfold dilution (*N*/10,000). This shows that any hydrolysis of the salt is inappreciable, as might have been expected.

Excess of Alkali.—The solution photographed was obtained by dissolving 0.0286 gram of trinitroacetaminophen in alcohol, adding alcoholic sodium hydroxide in excess of that required for maximum development of the purple shade, and making up to 100 c.c. with 96 per cent. alcohol. As 5 mm. of such a solution did

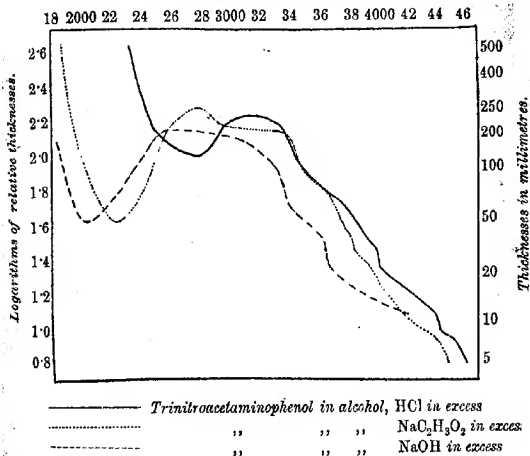
not given. The compound was dissolved in a 10% KOH solution, only the strong solution was used. The salt containing more than one atom of water is evidently strongly hydrolysed on dilution.

Methyl Ether = 2:3:5-Trinitro-4-acetylaminophenol,

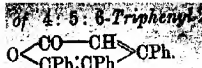


Attempts to methylate the trinitro-compound by silver oxide and methyl iodide led to negative results (Trans., 1909, 95, 1379). The

Oscillation frequencies.



solution of the silver salt described in this paper has, however, rendered possible the preparation of the above methyl ether and the corresponding trinitroanisidine. The silver salt in methyl-alcoholic solution is rapidly decomposed by methyl iodide, even at the ordinary temperature, the separation of silver iodide commencing soon after mixing the solutions and being complete after about half an hour's heating on the water-bath. Only about 15 per cent. of the trinitro-compound undergoes methylation in this process. The alcoholic solution, after filtration, is evaporated to a small volume, diluted with water, and extracted with an aqueous solution of



This substance is formed on adding deoxybenzoin (9.8 grams) to sodium ethoxide (3.4 grams) suspended in absolute ether, and then ethyl phenylpropionate (8.7 grams) to the solution which is promptly produced. The mixture becomes red, and a yellow solid separates. The reaction is complete in the course of a day; when then added, when part of the solid (8 grams) remains undissolved. This is insoluble in water or alcohol; it dissolves sparingly in ether, moderately in boiling, glacial acetic acid, and, on cooling, crystallises in faintly yellow prisms, which melt at 245—246°:

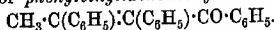
0.2030 gave 0.6342 CO₂ and 0.0930 H₂O. C=85.20; H=5.09.

C₂₃H₁₆O₂ requires C=85.18; H=4.94 per cent.

The yield of this substance is only 50 per cent. of the theoretical. This is due to the fact that part of the ethyl phenylpropionate is transformed into the acid, which, together with the unattacked deoxybenzoin, is contained in the ethereal layer from the product of the reaction.

Action of Potassium Hydroxide on Triphenyl-2-pyrone.

On boiling the pyrone with an excess of alcoholic potassium hydroxide on the water-bath, it dissolves, yielding a deep red solution, and finally a yellow solid. After four to five hours' heating, the alcohol is distilled off, water added to the residue, and the whole extracted with ether. On evaporation of the ether, a yellowish-red oil is left behind, which gradually sets almost completely, to a solid. This is washed with a little dilute alcohol, when it becomes quite white. This product is a mixture of the stereoisomerides of *phenylethylidenedeoxybenzoin*,



It readily dissolves in hot alcohol, and, on cooling, crystallises in colourless prisms, which begin to soften at 76°, and are completely melted at 90°:

0.1882 gave 0.6110 CO₂ and 0.1090 H₂O. C=88.54; H=6.13.

0.1970 „ 0.6400 CO₂ „ 0.1080 H₂O. C=88.60; H=6.09.

C₂₂H₁₈O requires C=88.59; H=6.04 per cent.

The substance is very soluble in carbon disulphide, and moderately so in light petroleum; it dissolves slowly in cold concentrated sulphuric acid, forming a red solution. I have repeatedly crystallised

the product from alcohol as well as from light petroleum, but all the fractions, on melting, showed practically the same behaviour, and on analysis, gave the same results.

The alkaline solution from the product of the action of potassium hydroxide on the pyrone, which contains a mixture of benzoic acid and the isomeric β -benzylcinnamic acids, is mixed with an excess of dilute sulphuric acid and repeatedly extracted with ether. On evaporation of the ether, a yellow oil is left behind, which sets to a solid after a few hours. When this is washed with cold dilute alcohol, β -benzylcinnamic acid remains undissolved.

β -Benzylcinnamic Acid, $C_6H_5 \cdot C(CH_2 \cdot C_6H_5) \cdot CH \cdot CO_2H$.

The acid is only sparingly soluble in cold alcohol, but readily so in boiling alcohol, and, on cooling, separates in long, colourless needles, which melt at $168-169^\circ$:

0.2028 gave 0.5992 CO_2 and 0.1080 H_2O . C=80.58; H=5.92.

$C_{16}H_{14}O_2$ requires C=80.64; H=5.88 per cent.

β -Benzylcinnamic acid is readily soluble in ammonia, and this solution, on the addition of silver nitrate, yields a white silver salt, which is sparingly soluble in boiling water:

0.2595 gave 0.0810 Ag. Ag=31.21.

$C_{16}H_{13}O_2Ag$ requires Ag=31.30 per cent.

β -Phenyl- β -benzylpropionic Acid, $C_6H_5 \cdot CH(CH_2 \cdot C_6H_5) \cdot CH_2 \cdot CO_2H$.

The reduction of β -benzylcinnamic acid readily takes place on dissolving it in dilute sodium hydroxide and shaking the solution with an excess of sodium amalgam ($2\frac{1}{2}$ per cent.) for about half an hour. The alkaline liquor is poured off and mixed with dilute hydrochloric acid, when an oil separates which solidifies in the course of a day. The solid is sparingly soluble in light petroleum, readily so in chloroform or alcohol; on adding water to the hot alcoholic solution until it becomes turbid, colourless prisms gradually separate, which melt at $95-96^\circ$:

0.1978 gave 0.5810 CO_2 and 0.1190 H_2O . C=80.10; H=6.71.

$C_{16}H_{16}O_2$ requires C=80.0; H=6.67 per cent.

The silver salt, which is formed on the addition of silver nitrate to the ammoniacal solution of the acid, is white, and does not change on drying in the water-oven:

0.2438 gave 0.0758 Ag. Ag=31.09.

$C_{16}H_{15}O_2Ag$ requires Ag=31.12 per cent.

On adding cold concentrated sulphuric acid to β -benzylcinnamic acid, the crystals gradually dissolve, forming a red solution which when kept overnight and then slowly poured into cold water, yields an oil. This gradually sets to a solid, which is sparingly soluble in boiling water, readily so in ether, chloroform, or alcohol; it is purified by adding water to the alcoholic solution until an emulsion is produced, from which light brown needles, melting at $100-101^\circ$ separate:

0.1883 gave 0.6023 CO_2 and 0.0950 H_2O . $\text{C}=87.23$; $\text{H}=5.60$.

$\text{C}_{16}\text{H}_{12}\text{O}$ requires $\text{C}=87.27$; $\text{H}=5.45$ per cent.

This compound is very soluble in alkalis, and does not give a colour reaction on the addition of ferric chloride to its alcoholic solution.

The alkaline solution, which is formed by the action of potassium hydroxide on triphenyl-2-pyrone, contains, besides β -benzylcinnamic acid, melting at $168-169^\circ$, its isomeride. This, being very soluble in alcohol, remains in the original alcoholic filtrate from the former acid, together with benzoic acid, which, also, is produced in the reaction. In order to remove the benzoic acid, water is added to the filtrate, and the whole extracted with ether. The product which is left behind on evaporation of the ether is distilled in a current of steam, the benzoic acid contained in the distillate is extracted with ether, and, after evaporation of the ether, re-crystallised from water. The isomeride of β -benzylcinnamic acid is not volatile with steam, and remains in the distilling flask as an oil, which slowly solidifies. The solid is very soluble in alcohol, ether, warm carbon disulphide, or chloroform, sparingly so in light petroleum. The solution in the latter solvent gradually deposits stout prisms, which soften at 104° , and are completely melted at 116° . That this substance is isomeric with β -benzylcinnamic acid, melting at 168° , is proved by the following analysis:

0.1900 gave 0.5620 CO_2 and 0.1023 H_2O . $\text{C}=80.67$; $\text{H}=5.98$.

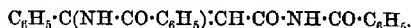
$\text{C}_{16}\text{H}_{14}\text{O}_2$ requires $\text{C}=80.64$; $\text{H}=5.88$ per cent.

The fact that this substance does not fuse sharply seems to indicate that it is not pure, but after repeated crystallisations from dilute alcohol or light petroleum, the behaviour on melting is practically unaltered.

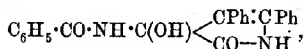
diketodiphenylpyrroline and its derivatives Part. III.

By SIEGFRIED RUHEMANN.

The formation of the diketodiphenylpyrrolines by the action of ethyl phenylpropionate on the sodium derivatives of aromatic amides is accompanied by the production of colourless compounds (see Ruhemann, *Trans.*, 1909, **95**, 984, 1603). One of these substances had been isolated previously (*loc. cit.*) from the product of the reaction of sodiobenzamide with the acetylenic ester, and its formula was found to be $C_{23}H_{18}O_3N_2$. With regard to its constitution, the view was expressed that this substance was the result of the union of benzamide with the first formed phenylpropionylbenzamide, and that, accordingly, it was represented thus:



A closer investigation, however, did not confirm this view; for the colourless substance, $C_{23}H_{18}O_3N_2$, on boiling with potassium hydroxide decomposes to yield deoxybenzoin, and with cold concentrated sulphuric acid breaks up quantitatively into diketodiphenylpyrroline and benzamide. This behaviour, and the fact that the compound has no basic properties, lead to the conclusion that it is to be regarded as an additive product of diketodiphenylpyrroline with benzamide. Its constitution, therefore, is to be expressed thus:



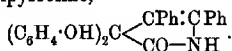
and it is therefore 3-benzoylamino-3-hydroxy-2-keto-4:5-diphenylpyrroline.

This result induced me to examine whether the diketopyrroline forms additive products with other substances, and in this respect, also, resembles isatin. It was found, indeed, that, like the latter compound (see Baumann, *Ber.*, 1885, **18**, 890), the diketopyrroline readily unites with phenylmercaptan to yield an additive compound, $C_{16}H_{11}O_2N, C_6H_5S$, which undoubtedly has a constitution similar to the additive product with benzamide, and which readily decomposes into its constituents, phenylmercaptan and the diketopyrroline. With piperidine, the diketopyrroline combines even in the cold to form the compound $C_{16}H_{11}O_2N, C_5H_{11}N$. This is more stable than the former substance, and does not decompose until its solutions in mineral acids are heated, when the diketopyrroline separates. The behaviour of piperidine towards isatin was examined

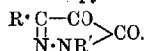
by Schott and others, and the reaction at the temperature of boiling concentrated sulphuric acid.



The resemblance between isatin and the diketopyrrolines is further indicated by the fact that they give the indophenol reaction. On shaking their solutions in concentrated sulphuric acid with benzene which contains thiophen, the red colour first changes to brown, and then gradually turns blue. Like isatin, diketodiphenylpyrroline condenses with phenol in the presence of concentrated sulphuric acid, and forms 2-keto-3:3-bis(hydroxyphenyl)-4:5-diphenylpyrroline,



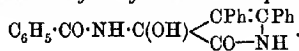
It may finally be stated that the relation which isatin exhibits to the diketopyrrolines as well as to the diketo-derivatives of cyclopentene extends also to the diketopyrazolines:



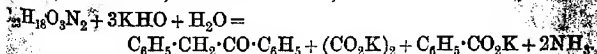
One member of this class of compounds, namely, 4:5-diketo-1-phenyl-3-methylpyrazoline, was first prepared by Knorr and Pschorr (*Annalen*, 1887, **238**, 194); afterwards Sachs and Barschall (*Ber.*, 1902, **35**, 1437; 1903, **36**, 1132) obtained diketopyrazolines by the action of nitrosodimethylaniline on the pyrazolones and subsequent treatment of the former condensation products with mineral acids. Up to the present, however, no member of this group of diketo-compounds is known in which the iminic hydrogen of the pyrazoline ring is intact. I propose to prepare such substances with the view of ascertaining whether they behave towards alkalis like their analogues and form blue salts.

EXPERIMENTAL.

3-Benzoylamino-3-hydroxy-2-keto-4:5-diphenylpyrroline,



On boiling this compound with an excess of concentrated potassium hydroxide, it decomposes and yields ammonia, decarbenzoin, oxalic acid, and benzoic acid, thus:



The heating was continued until ammonia ceased to be evolved:

steam was then passed through the product of the reaction, when a solid slowly passed over which, after crystallisation from light petroleum, melted at 60–61°. This substance was benzoylbenzoin:

0.1732 gave 0.5440 CO₂ and 0.0962 H₂O. C=85.66; H=6.17.

C₁₄H₁₂O requires C=85.71; H=6.12 per cent.

The remaining alkaline solution was treated with an excess of dilute sulphuric acid and subjected to steam distillation. The benzoic acid which is contained in the distillate was extracted with ether, recrystallised from water, and identified by the melting point. The formation of oxalic acid in the reaction was ascertained by the usual test.

The result of the action of potassium hydroxide on the colourless substance C₂₃H₁₈O₃N₂ indicates that it is an additive product of diketodiphenylpyrrolone with benzamide, and this conclusion is supported by the fact that, with sulphuric acid, the substance breaks up into these components. On adding the colourless compound to the concentrated acid, it dissolved, yielding a deep red solution. This, after being kept overnight, was gradually poured into cold water, and the diketodiphenylpyrrolone, which separated, was crystallised from dilute alcohol. It softens at 184°, and melts at 190–191° (instead of 184°, which was previously given as the melting point):

0.1948 gave 0.5505 CO₂ and 0.0820 H₂O. C=77.07; H=4.67.

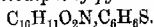
C₁₆H₁₁O₂N requires C=77.11; H=4.42 per cent.

The benzamide which is contained in the filtrate from the diketopyrrolone was extracted with ether, and, on evaporation of the ether, remained as a red solid, which, after crystallisation from water, melted at 130°:

0.2338 gave 24.2 c.c. N₂ at 18° and 754 mm. N=11.84.

C₇H₇ON requires N=11.57 per cent.

Additive Product of Diketodiphenylpyrrolone and Phenylmercaptan,



This additive product is readily formed on adding phenylmercaptan to the diketopyrrolone, dissolved in hot alcohol. The deep colour of the solution turns light red, and faintly pink plates soon separate. These were washed with ether and dried in a vacuum desiccator over sulphuric acid. The substance reddens at about 140°, and melts at 174–175°:

0.1760 gave 0.4755 CO₂ and 0.0785 H₂O. C=73.68; H=4.96.

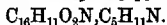
0.2240 „ 0.1476 BaSO₄; S=9.05.

C₂₀H₂₇O₂NS requires C=73.53; H=4.74; S=8.91 per cent.

On adding this compound to cold concentrated sulphuric acid,

heat is developed, the odour of phenylmercaptan is perceptible, and a deep red solution is produced, which yields a precipitate of diketodiphenylpyrroline when poured into water.

Additive Product of Diketodiphenylpyrroline and Piperidine,



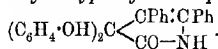
On adding piperidine to the diketopyrroline dissolved in ether, the red colour of the solution changes to yellow, and, after a short time, faintly brown, glistening prisms separate, which melt and decompose at 180—181°:

0.1632 gave 12.2 c.c. N_2 at 20° and 749 mm. $\text{N}=8.42$.

$\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2$ requires $\text{N}=8.38$ per cent.

The substance is rather stable towards mineral acids; decomposition into its constituents, the diketopyrroline and piperidine, does not take place until the solutions are heated.

2-Keto-3: 3-bishydroxyphenyl-4: 5-diphenylpyrroline,



Phenol reacts with diketodiphenylpyrroline under the same conditions as with isatin (see von Baeyer and Lazarus, *Ber.*, 1885, 18, 2641). The diketopyrroline (2 grams) was dissolved in an excess of phenol, and, gradually, concentrated sulphuric acid was added until the red colour of the solution turned deep brown. The whole was then poured into water, when a yellow, flocculent solid was precipitated. This was dissolved in ether, and the solution mixed with chloroform until it became turbid. In the course of a few hours, yellow plates separated, which retained their colour even on boiling the alcoholic solution with animal charcoal. The substance melts at 220—221°:

0.1600 gave 0.4697 CO_2 and 0.0755 H_2O . $\text{C}=80.06$; $\text{H}=5.24$.

0.2420 „ 7.2 c.c. N_2 at 17° and 747 mm. $\text{N}=3.39$.

$\text{C}_{23}\text{H}_{21}\text{O}_2\text{N}$ requires $\text{C}=80.19$; $\text{H}=5.01$; $\text{N}=3.34$ per cent.

This compound is sparingly soluble in chloroform or benzene, moderately so in ether or cold alcohol, but readily so in boiling alcohol. It dissolves in potassium hydroxide, yielding a yellow solution, from which it is precipitated unchanged on the addition of hydrochloric acid.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

The Constitution of Carpine. Part I.

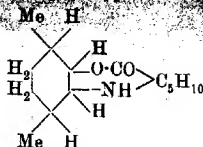
By GEORGE BARGER.

The alkaloid carpine was discovered by Greshoff in the leaves of the Papaw tree, *Carica Papaya*, L. (*Mededeelingen uit 's Lands Plantentuin*, No. 7, Batavia, 1890, p. 5). Merck (*Jahresber.*, 1891, p. 30) assigned to it the formula $C_{14}H_{27}O_2N$, but van Ryn (*Inaug. Diss. Marburg*, 1892; *Arch. Pharm.*, 1893, **231**, 184; 1897, **235**, 182) corrected this to $C_{14}H_{25}O_2N$. Van Ryn described a number of salts, and showed that carpine is a secondary base yielding a nitroso-derivative, $C_{14}H_{24}O_2N \cdot NO$, and that on methylation and ethylation a tertiary base and quaternary iodide are produced. He also attempted to obtain a knowledge of the constitution by oxidation with potassium permanganate, but his experiments in this direction were unsuccessful.

The alkaloid for the present investigation was prepared from Papaw leaves from British India; the yield was 0.07 per cent., or the same as that obtained by Greshoff from adult leaves (young leaves contain three to four times as much).

The experimental results which have been obtained so far show that carpine is the internal anhydride of a substance possessing both acid and basic properties, and closely resembling certain amino-acids; this substance contains a carboxyl group, and has the composition $C_{14}H_{27}O_3N$; the name *carpamic acid* is suggested for it. By oxidation with potassium permanganate, or preferably with nitric acid, a dibasic acid of the composition $C_8H_{14}O_4$ is formed, which is probably $\alpha\beta$ -dimethyladipic acid; this acid might result from the breaking down of a dimethylcyclohexane ring. Like carpine itself, the ethyl ester of carpamic acid yields a nitroso-derivative, whence it follows that the alkaloid cannot be a lactam, but must be a lactone, and that its two oxygen atoms are arranged as follows: $HO \cdot CO \cdot$. Although there is at present no direct evidence, it thus appears very probable that carpamic acid contains an alcoholic hydroxyl in addition to a carboxyl group and an imino-group; if attached to the cyclohexane ring, this hydroxyl would be converted on oxidation into one of the carboxyl groups of the acid $C_8H_{14}O_4$. In this case the carboxyl group of carpamic acid could not be directly connected to the cyclohexane ring, but would be attached to the rest of the molecule. The oxidation of carpine by potassium permanganate (see below) affords some evidence that the nitrogen atom is directly attached to the complex yielding the acid $C_8H_{14}O_4$, the rest of the molecule left unaccounted for is a bivalent group,

C_8H_{10} . The proposed largely hypothetical formula will serve to



show that if carpaïne contains 25 hydrogen atoms, there can only be one homocyclic ring, in addition to the lactone ring. With regard to the complex C_8H_{10} , nothing is known at present.

EXPERIMENTAL.

Composition and Properties of Carpaïne.

Van Ryn's analyses agree closely with the formula $C_{14}H_{25}O_2N$, and so far it was thought unnecessary to confirm this. It is, however, supported indirectly by the analyses of carpamic acid and its derivatives. Merck's formula, $C_{14}H_{27}O_2N$, is certainly incorrect, and the only other formula, $C_{14}H_{23}O_2N$, is hardly more likely.

The properties of carpaïne have been fully described by van Ryn, except the fact that the alkaloid can be distilled without decomposition. In a vacuum produced by charcoal and liquid air (the pressure was a fraction of a millimetre), 2 grams of carpaïne were distilled with the bath at $260-290^\circ$, and the vapour at $215-235^\circ$. The distillate crystallised in the receiver, and at once showed the melting point 121° (corr.), identical with that given by van Ryn.

Action of Acids on Carpaïne: Carpamic Acid.

Van Ryn attempted to hydrolyse carpaïne by boiling it with 1 per cent. alcoholic hydrogen chloride, but after twelve hours almost the whole of the alkaloid was recovered unchanged. This acid was much too dilute, and the temperature too low. When heated in a sealed tube to $130-140^\circ$ for a few hours with 10 per cent. hydrochloric or sulphuric acid, carpaïne is quantitatively changed to a substance containing one molecule of water more than carpaïne. The same change may be brought about more slowly by boiling with 20 per cent. hydrochloric acid. The completion of the change is best detected by the disappearance of the intensely bitter taste of carpaïne. When sulphuric acid has been used it may be removed with baryta, which does not precipitate the product of hydrolysis; in the case of hydrochloric acid, the excess of the acid can be removed by distillation under diminished pressure. The

hydrochloride of carpamine is obtained as a syrup, and crystallises on cooling. It may be crystallised from acetone, or by adding ether to its alcoholic solution, and forms needles melting at 161°.

0.1320 gave 0.2778 CO₂ and 0.1107 H₂O. C=57.4; H=9.3.

0.1270 „ 0.0627 AgCl. Cl=12.2.

C₁₄H₂₇O₃N.HCl requires C=57.2; H=9.5; Cl=12.1 per cent.

The free base may be obtained from the hydrochloride by decomposition with the calculated quantity of sodium carbonate, but as the substance is readily soluble in water and scarcely more soluble in alcohol than sodium chloride, it is difficult to obtain it quite free from salt by this means. It is therefore better to decompose the sulphate with baryta, or the hydrochloride with moist silver oxide, and to crystallise the residue left on evaporating the aqueous filtrate from dilute alcohol. It also crystallises very well on adding acetone to the cold alcoholic solution.

Carpamic acid, obtained in this manner, forms long needles, melting at 224°. Under a pressure of less than 1 mm., the substance sublimes unchanged; when heated under atmospheric pressure, it distils with slight decomposition:

0.1212 gave 0.2925 CO₂ and 0.1139 H₂O. C=65.8; H=10.4.

C₁₄H₂₇O₃N requires C=65.4; H=10.5 per cent.

The substance is optically active; in aqueous solution:

$l=1\text{-dcm.}; c=3.727; \alpha_D +0.26^\circ; [\alpha]_D +7.0^\circ.$

Carpamic acid is readily soluble in cold water, but only very sparingly so in alcohol; it is insoluble in acetone, ether, and most other organic solvents. The salts with mineral acids and with the alkali metals are readily soluble in water; the barium salt is a stiff jelly, so that the test-tube in which it is formed can be inverted. Carpamic acid has a hardly perceptible, faintly sweet taste, like some amino-acids; when pure and free from carpaine, the intense bitter taste of the latter alkaloid is absent. In dilute solution carpamic acid does not yield precipitates with potassium tri-iodide or with potassium mercuri-iodide, differing therein from carpaine; both bases, however, yield a precipitate with phosphomolybdic acid.

In solubilities, volatility, and chemical reactions, carpamic acid closely resembles certain amino-acids like leucine, but it has more definitely basic properties than are associated with α -amino-acids. The presence of a carboxyl group is demonstrated by esterification. Thus, when carpamic acid is suspended in absolute alcohol and treated with hydrogen chloride, there remains on evaporation of the acid a syrup, which crystallises on the addition of ether to its

concentrated solution of sodium formate, needles, melting at 171–172°, consisting of the hydrochloride of ethyl carpamate. 0.1354 gave 0.2968 CO₂ and 0.1178 H₂O. C=59.8; H=9.7.

C₁₆H₂₁O₃N.HCl requires C=59.7; H=9.9 per cent.

The same hydrochloride is formed almost quantitatively directly from carpaine by hydrolysis with alcoholic (instead of with aqueous) hydrochloric acid. For instance, 0.5 gram of carpaine, heated with 5 c.c. of 10 per cent. alcoholic hydrogen chloride for two hours to 160°, yielded 0.51 gram of this hydrochloride on addition of ether to its concentrated alcoholic solution.

The hydrochloride of ethyl carpamate is tasteless; its aqueous solution is precipitated by sodium carbonate. The free ester base is readily soluble in ether; it has not yet been crystallised.

From the above description it will be seen that carpaine and carpamic acid are related to each other in the same way as ergotinine and ergotoxine (Barger and Ewins, this vol., p. 284). Both carpaine and ergotinine are converted by acids in alcoholic solution into salts of an ester.

Action of Alkalis on Carpaine.

Carpaine is extremely resistant to alkalis. Thus, after 0.2 gram had been heated with 2 c.c. of 10 per cent. aqueous sodium hydroxide to 140–150° for three and a-half hours, 0.16 gram of carpaine was recovered unchanged. The carpaine was hardly attacked, because it is insoluble in water. In a similar experiment with 2 c.c. of 2.5*N*-sodium ethoxide, carpamic acid was formed, and when 0.2 gram had been heated to 180° for two hours with 4 c.c. of 3.3*N*-sodium ethoxide, 0.12 gram of carpamic acid was obtained. On fusion with alkali, a further change may take place. When 0.5 gram of carpaine was heated with 7 grams of potassium hydroxide and 0.5 c.c. of water, no apparent change took place below 300°. Then a dark brown solution was gradually formed, and, on cooling, hydrochloric acid yielded an oily precipitate soluble in ether with intense fluorescence. On evaporation, the ether left a red oil, which with ferric chloride yielded a reddish-brown coloration. It would appear that under these conditions a phenol is formed (by oxidation of a cyclohexane ring); a similar product was also obtained on chlorinating carpaine and treating the product with alkali (see below).

Further Degradation of Carpamic Acid.

This cannot readily be brought about by boiling with alkali. In the experiment 0.2 gram of carpamic acid was boiled with 6 c.c. of

50 per cent. potassium hydroxide solution. The potassium salt of the acid floated on top as a brown oil, and during half an hour's boiling very little, if any, of a volatile base was given off, corresponding at most to one-fiftieth of the nitrogen present. On cooling, the upper layer crystallised; it yielded, on acidification, unchanged carpamic acid.

By distilling carpamic acid with lime under diminished pressure, a little of an oily base is formed, insoluble in water, but soluble in ether. A similar base is formed on heating carpamic acid (or carpaine) with concentrated hydrochloric acid to 225–250°. In both cases the carboxyl group of carpamic acid seems to be eliminated, but neither reaction has been studied further for want of material.

Oxidation of Carpaine.

Carpaine is fairly resistant to oxidising agents. Van Ryn found that acid potassium permanganate is only very slowly decolorised at room temperature. By heating on the water-bath (in dilute sulphuric acid solution), oxidation was more rapid, and he obtained a mixture of crystalline, non-nitrogenous acids, the yield of which was, however, only 7½ per cent. of the alkaloid employed. By crystallisation from water, three fractions were obtained, melting continuously from 70–124°; the small yield of material available did not enable van Ryn to isolate any of the acids in a state of purity, and no analysis was made. The only other product obtained was ammonia.

In view of the difficulties encountered by van Ryn, it was thought advisable to modify the conditions of oxidation by using neutral potassium permanganate in acetone solution, a method which has of late yielded such good results in the case of brucine and strychnine (Leuchs, *Ber.*, 1908, **41**, 1711). Five grams of carpaine were dissolved in 125 c.c. of acetone, and 1.11 grams of finely powdered potassium permanganate (half an atomic proportion of oxygen) was added to the solution after cooling to 0°. The pink colour disappeared only very slowly. The solution was therefore warmed to room temperature, when the permanganate was completely reduced in a few hours. The same quantity was then again added; finally, when two atoms of oxygen had been used up, the solution was filtered, and was found to contain 2½–3 grams of the unchanged alkaloid.

In a second experiment 5 grams of carpaine in 140 c.c. of acetone were at once treated with 3.33 grams of potassium permanganate (=1½ atoms of oxygen); the temperature gradually rose from 23° to 37°, and then fell; the pink colour disappeared in half an hour. In all, 9 atoms of oxygen were supplied; the addition of per-

manganate, representing the last atom of oxygen, produced a rise of temperature only from 21—25°, and this time the pink colour persisted after seven hours. On filtration, the acetone was found to contain only a minute quantity of a neutral substance, melting at about 50°. The mixture of manganese dioxide and potassium salts was extracted with water (by shaking, glass beads being added). The pale brown solution was washed with ether, which did not remove an appreciable amount of substance; the solution was then acidified and became turbid; by repeated extracting with ether, 2.5 grams of a brown syrup were now obtained, but the aqueous solution still held in suspension a considerable quantity of a brown, oily substance, which was almost insoluble in ether. The syrup extracted by ether was esterified with methyl alcohol and hydrogen chloride, and was then distilled; between 110—120° at a pressure of 3—4 mm., there was collected a small quantity of a distillate, which was hydrolysed by boiling with potassium hydroxide; at the same time an alkaline gas (ammonia or an amine) was evolved. On acidification, 0.15 gram of an acid was obtained, which, on crystallisation from benzene, formed leaflets, melting not quite sharply at 98—100°. This acid was free from nitrogen, and was analysed:

0.0682 gave 0.1398 CO₂ and 0.0496 H₂O. C=55.9; H=8.1.

[C₈H₁₂O₄ requires C=55.8; H=7.0 per cent.]

C₈H₁₄O₄ „ C=55.2; H=8.0 „

The molecular weight was determined by the author's microscopic method (Trans., 1904, 85, 286):

0.0487, in 1.2744 grams methyl alcohol, was intermediate between 0.20 and 0.21 mol. benzil. M.W.=182—191, mean 186.

C₈H₁₄O₄ requires M.W.=174.

0.0164 gram of acid required for neutralisation 1.62 c.c. N/10-KOH, whence M.W. for a dibasic acid=204.

In the distillation of the ester a small quantity of a semi-solid fraction was further collected, boiling at 120—200°/3 mm., but the bulk of the material decomposed in the flask. It thus became evident that much more than 5 grams of the alkaloid would be required for the complete characterisation of the acid (van Ryn obtained no result from the oxidation of 10 grams with potassium permanganate). Other oxidising agents were therefore employed, and among these nitric acid was found to be much the most suitable. 0.2 Gram of carpaïne, heated in a sealed tube with 2 c.c. of nitric acid (D 1.41) to 140—170°, yielded only a minute quantity of an acid soluble in water, which on heating gave an odour similar to that of succinic anhydride; there was no trace of

an alkaloidal substance. The oxidation of carpaine was great pressure, most of the alkaloid having been oxidized to carbon dioxide. In a similar experiment with acid of density 1.32, 40 per cent. of a dibasic acid was obtained, and after a large number of such experiments the exact conditions were found for obtaining a mixture of non-nitrogenous acids weighing 75 per cent. of the alkaloid employed. This mixture is at present under investigation, and from it an acid of the composition $C_8H_{14}O_4$ has been isolated, which is probably a mixture of the two stereoisomeric forms of α -dimethyladipic acid, the same mixture having previously been obtained in very much smaller amount with potassium permanganate.

The oxidation of carpaine by halogens was also attempted. When chlorine is passed into a cold aqueous solution of the hydrochloride, the whole of the alkaloid is gradually precipitated as an amorphous chloro-derivative, which is decomposed by boiling alcohol, but can be crystallised from methyl alcohol (with considerable loss), forming leaflets, melting and decomposing at 77° :

0.0981 * gave 0.1854 CO_2 and 0.0618 H_2O . $C=51.7$; $H=7.0$.

0.1247 † „ 0.1132 $AgCl$. $Cl=22.5$.

$C_{14}H_{23}O_3NCl_2$ requires $C=51.8$; $H=7.1$; $Cl=21.9$.

This substance is neutral; two hydrogen atoms have been replaced by an oxygen atom and two chlorine atoms; it is therefore dichloro-oxy-carpaine, and as it is formed quantitatively, it was thought that it might form a suitable starting point for further degradation. The chlorine is very readily removed, by cold pyridine, for instance, but the substance is not simply a perchloride. A somewhat profound change has taken place; carpaine cannot be recovered from it, and by treatment with alkali a pink, fluorescent solution is obtained (benzene derivative?). So far it has been found impossible to obtain any further derivative in a pure state.

On passing chlorine into a solution of carpamic acid, a similar derivative is formed, which could not, however, be crystallised.

* Bromine produces in a solution of a carpaine salt an orange precipitate of a perbromide, from which carpaine is readily regenerated.

In comparing the oxidation by potassium permanganate in acetone solution with that by nitric acid at 130° , it should be noted that the latter reagent first hydrolyses the alkaloid to carpamic acid, which thus becomes open to attack. A non-nitrogenous acid is then formed, but potassium permanganate first produces a nitrogenous acid, which is only slightly soluble in ether. After dis-

* Crystallised.

† Amorphous, dried in a vacuum.

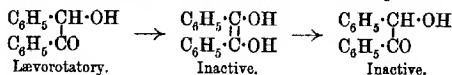
ylation of the acid with an amine or ammonia on hydrolysis and thus form $C_6H_5NH_2$ resulting. From this it would appear that the nitrogen atom is directly attached to the complex yielding this acid.

THE GOLDSMITHS' COLLEGE,
NEW CROSS, LONDON, S.E.

III.—Optically Active Glycols Derived from *l*-Benzoin and from Methyl *l*-Mandelate.

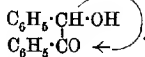
By ALEX. MCKENZIE and HENRY WREN.

The work described in the present communication was undertaken in consequence of the racemisation phenomena which were observed by one of us (Wren, Trans., 1909, 95, 1583, 1593) in connexion with the study of *l*-benzoin and its derivatives. *l*-Benzoin, which is prepared from magnesium phenyl bromide and *l*-mandelamide (McKenzie and Wren, Trans., 1908, 93, 312), has $[\alpha]_D -119^\circ$ in acetone solution, and undergoes complete racemisation with great readiness in the presence of alkali. The interpretation was suggested that the isomeric change in question was probably of a keto-enolic character, the hypothetical α -dihydroxystilbene being formed as an intermediate phase:



The racemisation of *l*-benzoin methyl ether also proceeds with great readiness in the presence of alkali.

In accordance with this view, the hydrogen attached to the carbon atom of the $:CH \cdot OH$ group migrates to the adjacent carbonyl-oxygen atom:



Desmotropic change of this nature is, however, impossible if the carbonyl group in *l*-benzoin is displaced by the $CRR \cdot OH$ group, a transformation which can be effected by the application of Grignard's reaction to *l*-benzoin. We find accordingly that optically active glycols of the types:

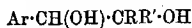
$C_6H_5 \cdot CH(OH) \cdot CRR \cdot OH$ and $C_6H_5 \cdot CH(OH) \cdot CRR \cdot OH$
do not lose their activity in the presence of alkali. The triphenyl

glycol, obtained from methyl *l*-mandelate and magnesium phenyl bromide, has $[\alpha]_D +221.3^\circ$ in acetone solution, and is perfectly stable, even when boiled with *N*/10-alcoholic potash for thirty minutes.

Similarly, the diphenylethyl glycol, obtained from *l*-benzoin and magnesium ethyl iodide, retains its activity unchanged during twenty-five hours at the ordinary temperature when dissolved in *N*/10-alcoholic potash, whereas *l*-benzoin methyl ether, under the same conditions, is racemised completely within five minutes.

The conversion of methyl *l*-mandelate, a highly active levorotatory compound with $[\alpha]_D -236^\circ$ in carbon disulphide solution (Wren, *loc. cit.*), into the highly active dextrorotatory triphenyl glycol, referred to above, suggested the possibility of a Walden inversion having occurred in this change. In order to obtain further evidence on this point, the action of magnesium phenyl bromide on *l*-benzoin was examined, when it was found that the resulting glycol was dextrorotatory and identical with the product from methyl *l*-mandelate. There is thus no evidence of a Walden inversion in either of these actions, and it is accordingly proposed to designate the dextrorotatory glycols, derived either from methyl *l*-mandelate or from *l*-benzoin, as *l*-compounds.

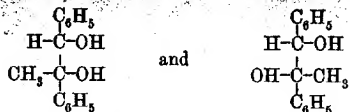
Desyl chloride has not yet been obtained in an optically active form, and we therefore treated *l*-benzoin with thionyl chloride, in the hope of obtaining an interesting compound in which the displacement of the chlorine by the hydroxy-group might be studied. Unfortunately, the product of the action was inactive desyl chloride. The displacement by the chlorine atom of the tertiary hydroxy-group in the active glycols, which are described in this paper, has not, so far, been attempted, since the action both of thionyl chloride and of fuming hydrochloric acid on inactive triphenylethylene glycol caused the elimination of one molecular proportion of water with the formation of triphenylvinyl alcohol. Now Tiffeneau (*Compt. rend.*, 1908, 146, 29) has found that the latter alcohol is also formed from triphenylethylene glycol by means of sulphuric acid; this behaviour is, however, abnormal, the researches of Tiffeneau showing that the elimination of water from the glycols of the type:



results in other cases in the formation of aldehydes of the type: $\text{ArRR}'\text{C}\cdot\text{CHO}$.

A further point arose in connexion with the interaction of *l*-benzoin and magnesium methyl iodide. Whilst the former compound contains only *one* asymmetric carbon atom, the carbon atom of the carbonyl group becomes asymmetric during this action, so that the formation

of two isomeric levorotatory glycols, each one of which contains two asymmetric carbon atoms, is theoretically possible:

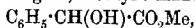


These glycols are not, of course, enantiomorphously related, and might be expected to be produced in unequal amounts. Only one isomeride was obtained. Again, when *r*-benzoin was acted on by magnesium methyl iodide, only one of the two possible inactive glycols was isolated, and it was obvious from the yield that the other isomeride could have been present only in small amount, or not at all.

The only glycol of the type $\text{R}\cdot\text{CH}(\text{OH})\cdot\text{CHR}\cdot\text{OH}$ known up to 1904 was the triphenylethylene glycol described by Gardeur (*Bull. Acad. roy. Belg.*, 1897, [iii], 34, 67). Acree (*Ber.*, 1904, 37, 2753) has shown that similar glycols are obtained by the aid of Grignard's action (compare also Tiffeneau and Dorlencourt, *Ann. Chim. Phys.*, 1909, [viii], 16, 237, and other papers). These compounds are all optically inactive. The Grignard action as applied to an ester of an optically active hydroxy-acid was studied for the first time by P. F. Frankland and Twiss (*Trans.*, 1904, 85, 1666), who prepared *d*-and-*l*-tetraphenylerythritol by the interaction of methyl *d*-tartrate and magnesium phenyl bromide. This ditertiary glycol is characterised by the high dextrorotation which it exhibits when contrasted with that of the tartrate from which it is derived.

In the course of the large amount of work carried out by many chemists on the connexion between unsaturated or negative groups and optical activity, the abnormal effects produced by the phenyl group have been repeatedly observed. It is, therefore, not surprising that such effects should be encountered with the compounds which are now described.

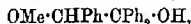
Purdie has shown that the substitution of the hydrogen atom of the alcoholic hydroxy-groups in the optically active lactic, malic, and tartaric acids (or their esters) by an alkyl group causes a very pronounced rise of optical activity. When a similar displacement is effected in *l*-mandelic acid, no such effect is observed (McKenzie, *Trans.*, 1899, 75, 753). Again, methyl *l*-mandelate,



has $[\alpha]_D - 236^\circ$ in carbon disulphide solution (Wren, *loc. cit.*), whereas methyl *l*-phenylmethoxyacetate, $\text{C}_6\text{H}_5\cdot\text{CH}(\text{OMe})\cdot\text{CO}_2\text{Me}$ (see experimental part) has $[\alpha]_D - 101.7^\circ$ in the same solvent. The com-

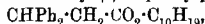
parison between the effect of the phenyl group, as brought about by the displacement of the hydroxy-group in *l*-mandelic acid (or its methyl ester) by the methoxy-group, and a similar displacement in aliphatic hydroxy-acids (or esters), leads to the conclusion that the great difference between the two cases is due to the influence exerted by the phenyl group.

When *l*-triphenylethylene glycol, $\text{OH}\cdot\text{CHPh}\cdot\text{CPh}_2\cdot\text{OH}$, is alkylated by means of silver oxide and methyl iodide, only one of the two hydroxy-groups undergoes methylation. It is shown that the mono-methoxy-derivative, obtained in this manner, has the formula

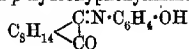


and not $\text{OH}\cdot\text{CHPh}\cdot\text{CPh}_2\cdot\text{OMe}$, and that the introduction of the methyl group into the molecule of the triphenyl glycol lowers the value for the specific rotation to $+185.3^\circ$ in acetone solution.

In a recent exhaustive study of the influence of constitution on the rotatory power of optically active compounds, Rupe (*Annalen*, 1909, 369, 311; compare also *ibid.*, 1903, 327, 157) points out that the *l*-menthyl esters of saturated acids, derived from phenylcinnamic acids, possess a higher degree of optical activity than the corresponding esters of the unsaturated acids. The normal effect which Rupe observed in this particular group appears to be that negative groups lower the rotatory power in a pronounced manner. Thus, in *l*-menthyl β -phenylcinnamate, $\text{CPh}_2\cdot\text{CH}\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_{19}$, with $[\alpha]_D -37.92^\circ$ in benzene solution, the optical effect caused by the asymmetric menthyl group is influenced by the electronegative character of two phenyl groups and of one double linking. When one of these negative factors is eliminated, for instance, the double linking, the rotatory power is enhanced, thus *l*-menthyl $\beta\beta$ -diphenylpropionate,



has $[\alpha]_D -61.72^\circ$ in benzene solution. Now this behaviour is opposed to the deduction from work of Tschugaeff, Haller, Walden, and others, and, indeed, also from Rupe's own work on this subject, namely, that unsaturated groups (phenyl group, double linking) tend to enhance optical rotation. For example, Rupe finds that *l*-menthyl crotonate has $[\alpha]_D -91.06^\circ$ in benzene solution, whereas *l*-menthyl *n*-butyrate has $[\alpha]_D -70.56^\circ$; the elimination of the double linking lowering the rotatory power in this case. Again, Frankland and Slator (*Trans.*, 1903, 83, 1349) show that *d*-tartranilide has a higher dextrorotation than has *d*-tartramide, and that aromatic groups raise the rotation of the latter compound very considerably. Finally another example of the same effect, and a very striking one, is the comparison between *p*-hydroxyphenyliminocamphor,



with [α]_D + 83° in chloroform solution, and the product of its reduction, 1-hydroxyphenylaminocamphor, $C_9H_{17}NO$, [α]_D + 83° in chloroform solution (Forster and Thornley, Trans. 1909, 95, 942).

In the course of his important work in this field, Rupe emphasizes the depression in rotation exerted by the displacement of a methyl by a phenyl group, thus:

<i>l</i> -Menthyl esters of the acids.	[α] _D in benzene solution.
$CH_3 \cdot CMe \cdot CO_2H$	- 81.76°
$CH_3 \cdot CPh \cdot CO_2H$	63.03
$CMe_2 \cdot CH \cdot CO_2H$	88.60
$CMePh \cdot CH \cdot CO_2H$	65.89
$CPh_2 \cdot CH \cdot CO_2H$	37.92

These figures are quoted here for comparison with the values obtained for the glycols:

<i>l</i> -Glycols.	[α] _D in acetone solution.
$OH \cdot CHPh \cdot CMe_2 \cdot OH$	- 21.8°
$OH \cdot CHPh \cdot CMePh \cdot OH$	+ 34.0
$OH \cdot CHPh \cdot CPh_2 \cdot OH$	+ 27.4
$OMe \cdot CHPh \cdot CPh_2 \cdot OH$	+ 185.3
$OH \cdot CHPh \cdot CPh_2 \cdot OH$	+ 221.8

The latter compounds are, of course, of a very different type from those of Rupe, and it is of interest that the effect of the phenyl group is so pronounced.

EXPERIMENTAL.

Action of Magnesium Methyl Iodide on l-Benzoin.

The Grignard reagent, prepared from 1.4 grams of magnesium (4 mols.), 7.8 grams of methyl iodide (4 mols.), and 50 c.c. of ether, was cooled in ice-cold water, and 3 grams of finely-powdered *l*-benzoin (1 mol.) were added in small quantities at a time. The action was vigorous. After the mixture had been boiled gently for three hours, it was decomposed in the usual manner by ice and dilute sulphuric acid, and the liberated glycol extracted with ether. After drying the ethereal solution and removing the ether, the resulting viscous, brown product solidified when stirred with a small quantity of carbon disulphide. It was purified by crystallising from carbon disulphide several times, 10 c.c. of solvent being used on each occasion, until its rotation was constant.

l-α-*Dihydroxy-αβ*-diphenylpropane, $OH \cdot CHPh \cdot CMePh \cdot OH$, separates from carbon disulphide as a colourless, amorphous solid, and melts at 81–82°. It is very readily soluble in boiling carbon disulphide, and sparingly so in the cold solvent. It is very readily soluble in cold benzene, methyl alcohol, ethyl alcohol, ether, or

acetone, and less so in cold carbon tetrachloride. It dissolves readily in boiling light petroleum (b. p. 60–80°), separating on cooling. It is very sparingly soluble in water. It gives a violet coloration with cold concentrated sulphuric acid.

For analysis, the glycol was dried at 78° until constant in weight:

0.1175 gave 0.3383 CO₂ and 0.0743 H₂O. C = 78.5; H = 7.1.

C₁₅H₁₆O₂ requires C = 78.9; H = 7.1 per cent.

The specific rotation was determined in acetone solution, the glycol having been dried at 78°:

$l = 2$, $c = 1.648$, $\alpha_D^{25} + 1.12^\circ$, $[\alpha]_D^{25} + 34.0^\circ$.

No racemisation was observed with the solution of the glycol in alcoholic potash.

Action of Magnesium Methyl Iodide on r-Benzoin.

Since a second asymmetric carbon atom is generated by the action of magnesium methyl iodide on benzoin, the behaviour of *r*-benzoin was studied in order to find out if only one glycol is formed. The experiment indicated that, if an isomeric glycol is produced, it can be present only in small amount.

Twelve grams of *r*-benzoin were gradually added to the Grignard reagent, prepared from 5.5 grams of magnesium, 30.3 grams of methyl iodide, and 100 c.c. of ether. The crude product, obtained as in the previous experiment, amounted to 12.5 grams. After one crystallisation from carbon disulphide, the glycol melted at 103.5–105.5°, and the yield was 11.5 grams. After a second crystallisation from the same solvent, the compound was pure.

Inactive $\alpha\beta$ -dihydroxy- $\alpha\beta$ -diphenylpropane separates from carbon disulphide in colourless needles, and melts at 103.5–104.5°. It is less soluble in carbon disulphide or light petroleum than is its *l*-isomeride. When dried in a vacuum over sulphuric acid at the ordinary temperature, it retains persistently small quantities of solvent. For analysis, it was accordingly dried at 78° until constant in weight:

0.1223 gave 0.3520 CO₂ and 0.0764 H₂O. C = 78.5; H = 7.0.

C₁₅H₁₆O₂ requires C = 78.9; H = 7.1 per cent.

The preparation of this glycol has also been described by Tiffeneau and Dorlencourt (*Ann. Chim. Phys.*, 1909, [viii], 16, 237), who give the melting point as 104°. There is also no evidence in the work recorded by these authors of the formation of a second isomeride.

Action of Magnesium Ethyl Iodide on l-Benzoin.

Four grams of *l*-benzoin (1 mol.) were treated with magnesium ethyl iodide, obtained from 1.8 grams of magnesium (4 mols.), 11.8 grams of

ethyl iodide (4 mols.), and 50 c.c. of ether. The crude diphenylethyl glycol (4.3 grams) was crystallised from successive small quantities of carbon disulphide. The first crop obtained melted sharply, and, when dried at 78° until constant in weight, gave the following value for its specific rotation in acetone solution:

$$l = 2, c = 1.288, \alpha_D^{20} + 0.64^\circ, [\alpha]_D^{20} + 24.8^\circ.$$

After a second crystallisation, the melting point was the same as before, but the value for the specific rotation determined as before was somewhat higher. The concentration, however, was greater:

$$l = 2, c = 4.674, \alpha_D^{20} + 2.56^\circ, [\alpha]_D^{20} + 27.4^\circ.$$

The value obtained after another crystallisation was practically identical with this.

1,2-Dihydroxy-2-diphenylbutane, $\text{OH} \cdot \text{CHPh} \cdot \text{C}(\text{EtPh}) \cdot \text{OH}$, separates from carbon disulphide in colourless prisms, capped by pyramids, and melts at 96.5—97.5°. It is very readily soluble in boiling carbon disulphide, and sparingly soluble in the cold solvent. It is soluble with difficulty in light petroleum or water. It is easily soluble in cold acetone, ethyl alcohol, benzene, chloroform, or ether, and less so in carbon tetrachloride. Its solution in cold concentrated sulphuric acid is magenta-coloured, and becomes green on heating.

For analysis, it was dried at 78°:

0.1509 gave 0.4366 CO_2 and 0.1018 H_2O . $\text{C} = 78.9$; $\text{H} = 7.5$.

$\text{C}_{16}\text{H}_{18}\text{O}_2$ requires $\text{C} = 79.3$; $\text{H} = 7.5$ per cent.

The value for the specific rotation in acetone solution is $+27.4^\circ$, as given above. In ethyl-alcoholic solution:

$$l = 2, c = 2.883, \alpha_D^{20} + 1.13^\circ, [\alpha]_D^{20} + 19.6^\circ.$$

In chloroform solution:

$$l = 4, c = 2.044, \alpha_D^{20} + 0.26^\circ, [\alpha]_D^{20} + 3.2^\circ.$$

The corresponding inactive compound has been prepared by Acree (*Amer. Chem. J.*, 1905, 33, 193). It melts at 115—116°.

When the *l*-glycol was dissolved in ethyl-alcoholic potassium hydroxide, no racemisation was detected. Thus 0.2977 gram, when made up to 10 c.c. in cold alcoholic potash (0.104*N*), had $\alpha_D + 1.20^\circ$ in a 2-dm. tube. This value did not alter during twenty-five hours at the temperature of the laboratory.

Action of Magnesium Phenyl Bromide on Methyl l-Mandelate and on l-Benzoin.

A solution of methyl *l*-mandelate (8 grams) in ether (50 c.c.) was siphoned within an interval of eight minutes into a solution of the Grignard reagent, prepared from magnesium (4.6 grams), bromobenzene

(30.3 grams) and ether (50 c.c.). The mixture had subsided, the mixture was boiled gently for two hours and then decomposed in the usual manner. The resulting brown solid was crystallised several times from methyl alcohol until its rotation was constant.

For analysis and determinations of its specific rotation, the glycol was dried at 100° until constant in weight. It retains methyl alcohol with considerable obstinacy, determinations indicating, however, that the alcohol is not present in the air-dried product in definite molecular proportions.

1- α - β -Dihydroxy- α - β -triphenylethane (triphenylethylene glycol),
 $\text{OH}\cdot\text{CHPh}\cdot\text{CPh}_2\cdot\text{OH}$,

separates from methyl alcohol in colourless needles, and, after being dried at 100°, melts at 128–129°, the melting point of the inactive isomeride being 167° according to Acree (*Ber.*, 1904, 37, 2762). The active glycol is readily soluble in boiling methyl alcohol. It may also be crystallised from light petroleum, in which it is sparingly soluble. It is practically insoluble in water, but dissolves with ease in cold acetone, benzene, ether, or chloroform. It gives an emerald-green coloration when heated with concentrated sulphuric acid; the solution becomes colourless in presence of excess of water, and a yellow tint appears when an excess of alkali is added. These colour reactions are also exhibited by triphenylvinyl alcohol:

0.1719 gave 0.5230 CO_2 and 0.0960 H_2O . C = 83.0; H = 6.2.

$\text{C}_{20}\text{H}_{18}\text{O}_2$ requires C = 82.7; H = 6.3 per cent.

A determination of its specific rotation in acetone solution gave the result:

$l = 4$, $c = 1.0156$, $\alpha_D^{20} + 8.99^\circ$, $[\alpha]_D^{20} + 221.3^\circ$.

Its rotation was also determined in chloroform solution:

$l = 4$, $c = 1.3196$, $\alpha_D^{15} + 12.33^\circ$, $[\alpha]_D^{15} + 233.6^\circ$.

It was of interest to find out if a dextrorotatory glycol would also be obtained by the interaction of *l*-benzoin and magnesium phenyl bromide. Finely-powdered *l*-benzoin (3 grams) was accordingly added gradually to the solution obtained from magnesium (1 gram), bromobenzene (8.1 grams), and ether (60 c.c.), the Grignard reagent having been cooled previously in ice-cold water. After the addition of the benzoin, the mixture was boiled gently for ninety minutes. The glycol was isolated as in the preceding experiment. On analysis:

0.1343 gave 0.4085 CO_2 and 0.0758 H_2O . C = 82.95; H = 6.3.

$\text{C}_{20}\text{H}_{18}\text{O}_2$ requires C = 82.7; H = 6.3 per cent.

The compound was identical with that obtained from methyl mandelate, as shown by determinations of melting point and specific rotation made with it.

The action of thionyl chloride on desyl chloride was examined. Triphenylmethyl glycol (0.8 gram) was heated for thirty minutes in 25 c.c. of 0.112*N* alkali. A violet coloration appeared at first, and when the solution was shaken, this became reddish-brown. The mixture was poured into 200 c.c. of water, and the precipitated glycol filtered and dried. Polarimetric examination in acetone solution showed that the glycol had remained unracemised even after this drastic treatment with alkali.

Action of Magnesium Methyl Iodide on Methyl l-Mandelate.

A solution of methyl *l*-mandelate (7 grams) in ether (40 c.c.) was siphoned within an interval of ten minutes into an ice-cold solution of the Grignard reagent, prepared from magnesium (4.4 grams), methyl iodide (26.1 grams), and ether (50 c.c.). The crude product obtained in the usual manner was an oil, which was dried and obtained crystalline by being stirred with light petroleum. After two further crystallisations from light petroleum containing a little ether, the glycol was obtained pure.

1- $\alpha\beta$ -Dihydroxy- α -phenylisobutane, $\text{OH}\cdot\text{CHPh}\cdot\text{CMe}_2\cdot\text{OH}$, melts at 33.5–35°. It gives an orange coloration with cold concentrated sulphuric acid, and the solution becomes strongly fluorescent when warmed:

0.2657 gave 0.7000 CO_2 and 0.2029 H_2O . $\text{C} = 71.9$; $\text{H} = 8.5$.

$\text{C}_{10}\text{H}_{14}\text{O}_2$ requires $\text{C} = 72.2$; $\text{H} = 8.5$ per cent.

Its specific rotation was determined in acetone solution:

$l = 2$, $c = 2.7352$, $\alpha_D^{15} = -1.18^\circ$, $[\alpha]_D^{15} = -21.6^\circ$.

Action of Thionyl Chloride on l-Benzoin and on Inactive Triphenylethylene Glycol.

The action of thionyl chloride on *l*-benzoin was studied in the hope of obtaining optically active desyl chloride, but racemisation occurred in the displacement of the hydroxy-group by chlorine. *l*-Benzoin (3.2 grams) was covered with thionyl chloride (3.5 grams). The evolution of hydrogen chloride began at the ordinary temperature, whilst the product gradually became liquid. After three hours, the temperature was raised gradually from 15° to 55° during the course of two hours, when very little action appeared to take place. At 55° hydrogen chloride was again evolved somewhat briskly. The temperature was then raised to 90°. The dark reddish-brown liquid became semi-solid when placed over soda-lime in a vacuum. After some days, the specific rotation of the product in acetone solution was -9.7° , but this activity may have been due to a little unchanged

benzoin. After three crystallisations from ethyl alcohol, desyl chloride, melting at $66-68^{\circ}$, was obtained. This was quite inactive when examined polarimetrically.

Thionyl chloride (28 grams) was added to inactive triphenylethylene glycol (5 grams) prepared from *r*-benzoin according to Acree (*loc. cit.*). The glycol dissolved within fifteen minutes at the ordinary temperature, the red solution slowly evolving hydrogen chloride. The temperature was raised slowly to the boiling point of thionyl chloride during one hour, and maintained at this point for two hours longer. After drying over soda-lime in a vacuum, the resulting solid was crystallised twice from light petroleum (b. p. $60-80^{\circ}$). The compound obtained in this manner was quite free from chlorine, and its melting point ($135-136^{\circ}$) and analysis showed that it was triphenylvinyl alcohol:

0.1654 gave 0.5352 CO_2 and 0.0889 H_2O . $\text{C} = 88.2$; $\text{H} = 6.0$.

$\text{C}_{20}\text{H}_{16}\text{O}$ requires $\text{C} = 88.2$; $\text{H} = 5.9$ per cent.

Triphenylvinyl alcohol has been prepared by Delacre (*Bull. Soc. chim.*, 1895, [iii], 13, 857; compare also Saint-Pierre, *Bull. Soc. chim.*, 1891, [iii], 5, 292; Gardeur, *Bull. Acad. roy. Belg.*, 1897, [iii], 34, 67), who employed the Friedel-Crafts' reaction with trichloroacetyl chloride and benzene. The proof, however, that the compound in question was triphenylvinyl alcohol, CPh_2CPhOH , and not triphenylethanone, CHPh_2COPh , was supplied by Biltz (*Ber.*, 1899, 32, 650). Anschütz and Förster (*Annalen*, 1909, 368, 89) have observed recently that triphenylvinyl alcohol is formed by the interaction of acetylmandelyl chloride, benzene, and aluminium chloride, whereas the formation of benzoin acetate might have been expected. The same authors also prepared the vinyl alcohol from desyl chloride, benzene, and aluminium chloride.

The action of fuming hydrochloric acid on inactive triphenylethylene glycol is similar to that of thionyl chloride. Three grams of the glycol were added to 40 c.c. of aqueous hydrochloric acid, saturated at 0° . After several weeks in a stoppered bottle at the ordinary temperature, the product was diluted with water, and the solid crystallised twice from ethyl alcohol. It melted at $135.5-136.5^{\circ}$, and when it was mixed with an equal amount of the glycol, obtained by the aid of thionyl chloride, the melting point did not change.

Inactive β -Hydroxy- α -methoxy- $\alpha\beta$ -triphenylethane.

Methylation of Inactive Triphenylethylene Glycol.—Four grams of the inactive glycol (1 mol.) were added to 9.6 grams of silver oxide (3 mols.), 24 grams of methyl iodide (12 mols.), and 35 c.c. of acetone. The mixture was boiled gently for six hours and filtered. The solvent

was removed from the filtrate, and the product again alkylated with half the above quantities of oxide and iodide. The product obtained in this manner was crystallised once from much light petroleum (b. p. 60–80°), and then twice from methyl alcohol :

0.1166 gave 0.3557 CO₂ and 0.0875 H₂O. C = 83.2 ; H = 6.5.

0.3284 „ 0.2392 AgI ; OMe = 9.6.

C₂₁H₂₀O₂ requires C = 82.9 ; H = 6.6 ; OMe = 10.2 per cent.

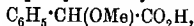
This compound is obviously a monomethyl derivative of triphenyl-ethylene glycol. The following experiments showed that it was β -hydroxy- α -methoxy- $\alpha\beta$ -triphenylethane, and not α -hydroxy- β -methoxy- $\alpha\beta$ -triphenylethane.

Action of Magnesium Phenyl Bromide on Inactive Benzoïn Methyl Ether.—The Grignard reagent, prepared from 0.4 gram of magnesium (1.3 mols.), 2.5 grams of bromobenzene (1.3 mols.), and 14 c.c. of ether, was boiled gently for two hours with 2.7 grams of inactive benzoïn methyl ether (1 mol.). The product, obtained in the usual manner, was a crystalline solid, and amounted to 3.2 grams. After two crystallisations from much ethyl alcohol, β -hydroxy- α -methoxy- $\alpha\beta$ -triphenylethane, melting at 139°, was obtained. Its identity with the compound prepared from triphenylethylene glycol was shown by the melting point of a mixture of the two, and by the analysis :

0.1818 gave 0.5510 CO₂ and 0.1080 H₂O. C = 82.65 ; H = 6.6.

C₂₁H₂₀O₂ requires C = 82.9 ; H = 6.6 per cent.

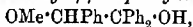
Action of Magnesium Phenyl Bromide on Inactive Methyl Phenyl-methoxyacetate.—Inactive phenylmethoxyacetic acid,



was prepared by the interaction of sodium methoxide and methyl phenylchloroacetate. It was isolated by the aid of its sparingly soluble sodium salt (compare McKenzie, Trans., 1899, 75, 753), and then esterified by means of methyl alcohol and sulphuric acid. Eighteen grams of methyl ester, boiling at 118–119°/8 mm., were obtained from 20 grams of acid.

Five grams of the methyl ester (1 mol.), dissolved in 40 c.c. of ether, were added to a solution of 2 grams of magnesium (3 mols.) in 13.2 grams of bromobenzene (3 mols.) and 40 c.c. of ether within an interval of six minutes. The crude product obtained by decomposition of the additive compound was crystallised twice from ethyl alcohol. The yield of pure methoxy-glycol amounted to 5.4 grams. It was identical with the products obtained from triphenylethylene glycol and benzoïn methyl ether respectively.

Inactive β -hydroxy- α -methoxy- $\alpha\beta$ -triphenylethane,



melts at 138.5–139.5°. It is fairly soluble in boiling ethyl alcohol,

and sparingly so in the cold. It crystallises from ethyl alcohol in colourless prisms. It may also be crystallised from light petroleum (b. p. 60–80°), in which it is fairly soluble on heating. It is fairly soluble in cold ether, easily so in cold acetone or chloroform, somewhat less readily so in cold carbon tetrachloride, and sparingly soluble in water. It gives a colour reaction with concentrated sulphuric acid similar to that of *l*-triphenylethylene glycol.

1-β-Hydroxy-α-methoxy-αββ-triphenylethane.

Action of Magnesium Phenyl Bromide on Methyl 1-Phenylmethoxyacetate.—Methyl *l*-mandelate was alkylated with silver oxide and methyl iodide, the mixture of methoxy-ester and unchanged methyl mandelate saponified, and the resulting acid converted into sodium salt. Since sodium *l*-phenylmethoxyacetate is sparingly soluble in water (McKenzie, *loc. cit.*), it can be separated readily from the sodium mandelate present.

l-Phenylmethoxyacetic acid, obtained from the sodium salt, had $[\alpha]_D^{25} - 150.1^\circ$ for $c = 3.597$ in ethyl-alcoholic solution, the value quoted previously being $[\alpha]_D^{25} - 150.0^\circ$ for $c = 6.7656$.

l-Phenylmethoxyacetic acid (10 grams) was converted into its methyl ester by the Fischer-Speier method, using methyl alcohol and sulphuric acid. The yield was 8.5 grams.

Methyl 1-phenylmethoxyacetate, $C_6H_5 \cdot CH(OMe) \cdot CO_2Me$, is a colourless oil, which boils at 117.5–118°/8 mm.:

0.2885 gave 0.6988 CO_2 and 0.1775 H_2O . C = 66.1; H = 6.9.

$C_{10}H_{12}O_3$ requires C = 66.6; H = 6.7 per cent.

The following determinations of specific rotation of this ester in various solvents were made for comparison with the activity of methyl *l*-mandelate in carbon disulphide solution:

$l = 1$, $c = 2.93$, $[\alpha]_D^{25} - 2.98^\circ$, $[\alpha]_B^{25} - 101.7^\circ$.

In acetone solution:

$l = 4$, $c = 2.6948$, $\alpha_D^{15} - 10.38^\circ$, $[\alpha]_D^{15} - 96.3^\circ$.

In benzene solution:

$l = 4$, $c = 2.0968$, $\alpha_D^{20} - 8.32^\circ$, $[\alpha]_D^{20} - 99.2^\circ$.

A solution of methyl *l*-methoxymandelate (5 grams, 1 mol.) in ether (40 c.c.) was siphoned with constant shaking within an interval of six minutes into a solution of the Grignard reagent (3 mols.) prepared from magnesium (2 grams), bromobenzene (13.2 grams), and ether (40 c.c.). Towards the end of the addition a bulky precipitate separated, which became grey on warming. The mixture was heated for two hours. The crude product resulting from the action amounted

to 9 grams. After two crystallisations from ethyl alcohol, the compound is pure.

l- β -Hydroxy- α -methoxy- $\alpha\beta$ -triphenylethane, $\text{OMe} \cdot \text{CHPh} \cdot \text{CPh}_2 \cdot \text{OH}$, separates from ethyl alcohol in colourless needles, grouped in rosettes, and melts at $143\text{--}144^\circ$. Its colour reaction with concentrated sulphuric acid is similar to that of the inactive isomeride:

0.1459 gave 0.4423 CO_2 and 0.0852 H_2O . $\text{C} = 82.7$; $\text{H} = 6.5$.

0.2397 „ 0.1742 AgI. $\text{OMe} = 9.6$.

$\text{C}_{21}\text{H}_{20}\text{O}_2$ requires $\text{C} = 82.9$; $\text{H} = 6.6$; $\text{OMe} = 10.2$ per cent.

Its specific rotation was determined in a number of solvents. In acetone solution:

$$l = 1, c = 5.428, \alpha_D^{12} + 10.06^\circ, [\alpha]_D^{12} + 185.3^\circ.$$

In chloroform solution:

$$l = 1, c = 4.579, \alpha_D^{12} + 10.76^\circ, [\alpha]_D^{12} + 235.0^\circ.$$

In benzene solution:

$$l = 1, c = 3.667, \alpha_D^0 + 10.8^\circ, [\alpha]_D^0 + 294.5^\circ.$$

In ethyl-alcoholic solution:

$$l = 4, c = 1.0176, \alpha_D^0 + 6.77^\circ, [\alpha]_D^0 + 166.3^\circ.$$

The glycol is sparingly soluble in cold ethyl alcohol. It may also be crystallised from methyl alcohol or light petroleum (b. p. $60\text{--}80^\circ$). It is easily soluble in cold acetone, chloroform, carbon tetrachloride, ether, or benzene, and sparingly so in water.

Methylation of l-Triphenylethylene Glycol.—Seven grams of *l*-triphenylethylene glycol (1 mol.) were heated with 11.2 grams of silver oxide (2 mols.), 42 grams of methyl iodide (12 mols.), and 10 c.c. of acetone during seven hours. The alkylation was found, however, to be incomplete even after a second alkylation under the same conditions as before. After a third alkylation, the product was crystallised until its rotation was constant, four crystallisations from light petroleum being necessary. The glycol obtained in this manner was identical with *l*- β -hydroxy- α -methoxy- $\alpha\beta$ -triphenylethane described above. It melted at $143\text{--}144^\circ$, and its identity was confirmed by the mixed melting-point method. A determination of its specific rotation in acetone solution gave the result:

$$l = 2, c = 2.885, \alpha_D^{13} + 10.68^\circ, [\alpha]_D^{13} + 185.1^\circ.$$

No racemisation was detected with the solution of this glycol in alcoholic potash. 0.254 Gram was made up to 25 c.c. with 0.168*N*-alkali. This solution gave $\alpha_D + 6.84^\circ$, a value which had not changed after twenty hours at the ordinary temperature.

The bulk of the expense of this investigation has been defrayed by grants from the Government Grant Committee of the Royal Society and from the Research Fund Committee of the Chemical Society, for which we desire to make this grateful acknowledgment.

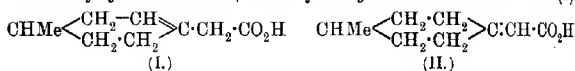
BIRKBECK COLLEGE,
LONDON, E.C.

III.—The Synthesis of Δ^1 -cyclopenteneacetic Acid and 1-Methyl- Δ^2 -cyclohexene-3-acetic Acid.

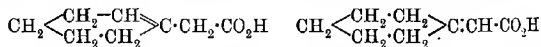
By VICTOR JOHN HARDING and WALTER NORMAN HAWORTH.

A SHORT time ago, Harding, Haworth, and Perkin (Trans., 1908, 93, 1943) published an account of a series of experiments on the constitution and synthesis of 1-methylcyclohexylidene-4-acetic acid. In the course of this investigation a convenient method for the preparation of unsaturated cyclic acids was discovered, and the present authors have continued the work in this direction.

In the previous communication (*loc. cit.*) it was shown that the condensation of ethyl sodiocyanoacetate with cyclohexanone and 1-methylcyclohexan-4-one gave products which, on hydrolysis, yielded derivatives of acetic acid containing the double bond in the ring. In the case of 1-methylcyclohexan-4-one, 1-methyl- Δ^3 -cyclohexene-4-acetic acid (I)



is produced. The isomeric 1-methylcyclohexylidene-4-acetic acid (II), an acid first prepared by Perkin and Pope (Trans., 1908, 93, 1075; compare also Wallach, *Annalen*, 1909, 365, 266), is not formed in any appreciable quantity. The products of the condensation of cyclohexanone and ethyl sodiocyanoacetate were also investigated, and it was shown that in this case a mixture of the two isomeric acids:



was produced (Harding, Haworth, and Perkin, *loc. cit.*, p. 1961), the latter acid being present, however, only in small amount.

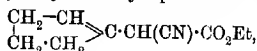
This fact is worthy of note, since there is no evidence of the formation, even in traces, of 1-methylcyclohexylidene-4-acetic acid during the condensation of 1-methylcyclohexan-4-one and ethyl sodiocyanoacetate.

It is clear that in the latter case the cyano-ester obtained from the cyclic ketone and ethyl cyanoacetate, whether piperidine or sodium ethoxide is used as the condensing agent, consists almost entirely of

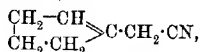
the derivative with the double linking in the ring. This was further proved by the observation that, when treated with methyl iodide or bromoacetophenone, substitution derivatives were readily formed (*loc. cit.*, p. 1958) in almost quantitative yield. In the present communication the authors have extended their investigation to *cyclopentanone* and inactive 1-methylcyclohexan-3-one.

The condensation products of *cyclopentanone* are particularly interesting, because in this case the resulting ester is solid, whereas in the case of six-membered rings it is a liquid. This fact has enabled the authors to remove all doubt as to the nature of the reaction, since they have found that, prepared either by means of ethyl sodiocyanoacetate or the free ester and piperidine, the cyano-ester obtained is the same.

cyclopentanone condenses readily with ethyl sodiocyanoacetate with the formation of ethyl α -cyano- Δ^1 -cyclopentene-1-acetate,

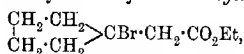


and α -cyano- Δ^1 -cyclopentene-1-acetic acid. The methyl ester is obtained in a similar manner from methyl sodiocyanoacetate and *cyclopentanone*, and is also crystalline. Both these cyano-esters may be methylated by treatment with sodium methoxide and methyl iodide. α -Cyano- Δ^1 -cyclopentene-1-acetic acid decomposes on distillation under diminished pressure with elimination of carbon dioxide and formation of Δ^1 -cyclopenteneacetonitrile,

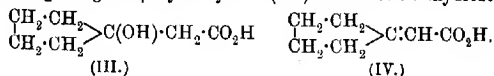


from which, by digestion with alcohol and sulphuric acid and subsequent hydrolysis, Δ^1 -cyclopenteneacetic acid is obtained.

This acid had previously been prepared by Wallach (*Annalen*, 1902, 323, 159, and 1906, 347, 324), who obtained it by the condensation of *cyclopentanone* and ethyl bromoacetate in presence of zinc, and subsequent elimination of water from the hydroxy-ester by means of potassium hydrogen sulphate. When the hydroxy-ester is treated with hydrobromic acid it yields ethyl 1-bromocyclopentane-1-acetate,

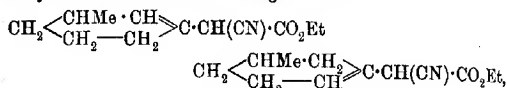


and this is decomposed by dimethylaniline with the formation of ethyl Δ^1 -cyclopenteneacetate. In order to remove all doubt as to the constitution of this acid, the authors have, with the kind permission of Prof. O. Wallach, prepared the isomeric *cyclopentylideneacetic acid* (IV) by digesting the β -hydroxy-acid (III) with acetic anhydride:

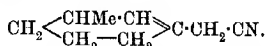


The latter acid yields cyclopentanone on oxidation with alkaline permanganate, and its formation by the above method is exactly similar to that of 1-methylcyclohexylidene-4-acetic acid from 1-methyl-4-hydroxycyclohexane-4-acetic acid.

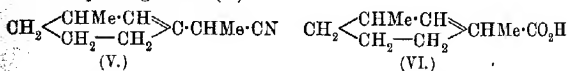
The condensation of 1-methylcyclohexan-3-one with ethyl sodio-cyanoacetate proceeds quite readily, with the formation of an ester which may have either of the following constitutions:



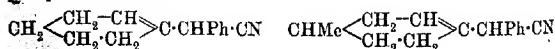
and it has not yet been found possible to decide between these, but in this paper we assume that it has the former. The cyano-acid obtained from the hydrolysis of this ester loses carbon dioxide when distilled under diminished pressure, with the production of 1-methyl- Δ^2 -cyclohexene-3-acetonitrile.



When this nitrile is hydrolysed it yields the corresponding acid, which was found to melt at 25° . Wallach (*Annalen*, 1901, 314, 157; 1906, 347, 340), by the condensation of 1-methylcyclohexan-3-one with ethyl bromoacetate in presence of zinc, and the subsequent elimination of water from the hydroxy-ester, obtained a liquid acid, the amide of which he first found to melt at 150° , but in a later paper he gives $153-154^\circ$ as the true melting point. The amide of the acid which we have prepared was found to melt at 150° , but we do not think there can be any doubt as to the identity of the two acids. The possibility that this acid contains the ethylenic linking outside the ring, and is, therefore, 1-methylcyclohexylidene-3-acetic acid, may be dismissed, since the cyano-ester, from which it is produced readily, gives on treatment with sodium methoxide and methyl iodide a methyl-substituted derivative which passes on hydrolysis and distillation into the corresponding nitrile (V).

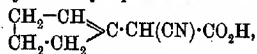


This nitrile can be further hydrolysed only with difficulty to the corresponding α -1-methyl- Δ^2 -cyclohexene-3-propionic acid (VI), which is a liquid. The authors have also attempted to prepare alicyclic phenyl-acetic acids by condensing cyclohexanone and 1-methylcyclohexan-4-one with phenylacetonitrile in the presence of sodium ethoxide. The phenylacetonitriles:



are easily obtained in this way, but, so far, no method by which they can be hydrolysed to the corresponding acids has been found. All attempts to hydrolyse these nitriles resulted in the production of the original ketone and phenylacetic acid.

EXPERIMENTAL.

 α -Cyano- Δ^1 -cyclopenteneacetic Acid,

and its Ethyl Ester.

In preparing ethyl α -cyano- Δ^1 -cyclopenteneacetate, ethyl cyanoacetate (56 grams) was added to a solution of sodium (11.5 grams) in alcohol, and, after the separation of the white sodium derivative, cyclopentanone (42 grams) was then introduced. The sodium derivative rapidly dissolved, leaving a clear solution, which was heated for an hour on the water-bath, and the yellow solid which had separated was dissolved in water and decomposed by dilute hydrochloric acid. The precipitated oil was extracted with ether, the ethereal solution washed with water, and then shaken with sodium carbonate, dried, and evaporated. The residual oil on fractionation yielded a small quantity of cyclopentanone, and then ethyl α -cyano- Δ^1 -cyclopenteneacetate distilled over at 163–165°/15 mm. as a viscous, colourless oil which, when pure, solidified in colourless needles, melting at 54°:

0.1230 gave 0.3021 CO_2 and 0.0811 H_2O . C = 67.0; H = 7.3.

0.1373 „ 9.1 c.c. N_2 at 16° and 761 mm. N = 7.7.

$\text{C}_{10}\text{H}_{18}\text{O}_2\text{N}$ requires C = 67.0; H = 7.3; N = 7.8 per cent.

The sodium carbonate extract on acidifying yielded an oil which was extracted with ether, and, after evaporation of the solution, the residue rapidly solidified. The solid acid was pressed on porous porcelain, and then recrystallised from benzene, or, better, from anhydrous ether, from which it separates in large, colourless prisms, melting at 129°:

0.1301 gave 0.3029 CO_2 and 0.0682 H_2O . C = 63.4; H = 5.8.

0.1020 „ 8.0 c.c. N_2 at 18° and 760 mm. N = 9.1.

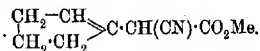
$\text{C}_8\text{H}_{10}\text{O}_2\text{N}$ requires C = 63.5; H = 5.9; N = 9.3 per cent.

α -Cyano- Δ^1 -cyclopenteneacetic acid is soluble in ether, benzene, ethyl acetate, or ethyl alcohol, but only sparingly so in light petroleum. It dissolves in dilute potassium hydroxide, and the solution soon clouds on warming, owing to the separation of cyclopentanone by decomposition of the acid. The potassium salt is sparingly soluble in concentrated alkali.

The following is an alternative method of preparation with the aid of piperidine:

Equimolecular quantities of cyclopentanone and ethyl cyanoacetate were mixed with a few drops of piperidine, and the whole kept cold for four hours; the condensation was completed by warming on the water-bath for an hour. The product was cooled and poured into water, when ethyl α -cyano- Δ^1 -cyclopenteneacetate separated as a brown, crystalline solid, which was collected, freed from oil by porous porcelain, and recrystallised from dilute ethyl alcohol, from which it separates in tufts of fine, silky needles, melting at 53–54°, the yield by this method being almost quantitative.

Preparation of Methyl α -Cyano- Δ^1 -cyclopenteneacetate,



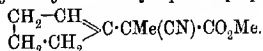
(a) *With Sodium Methoxide.*—cyclopentanone (8 grams) was added to methyl sodiocyanoacetate (12 grams), prepared in methyl-alcoholic solution, and the mixture was shaken and gently warmed for ten minutes. Water and dilute mineral acid were then added, and the oil was extracted with ether, washed with sodium carbonate, dried, and distilled, when methyl α -cyano- Δ^1 -cyclopenteneacetate passed over as a colourless oil, boiling at 152°/17 mm. The ester gradually crystallised, on keeping overnight, in colourless crystals, melting at 35°; it is soluble in most organic solvents, and is easily recrystallised from dilute methyl alcohol.

(b) *With Piperidine.*—Equimolecular proportions of cyclopentanone and methyl cyanoacetate were mixed with a few drops of piperidine, and the condensation was complete at the end of four hours. The product was poured into water, extracted with ether, and treated exactly as described under (a). The product was identical in every respect with that prepared by method (a):

0.1682 gave 11.8 c.c. N_2 (moist) at 14° and 740 mm. $\text{N} = 8.3$.

$\text{C}_9\text{H}_{11}\text{O}_2\text{N}$ requires $\text{N} = 8.5$ per cent.

Methyl α -Cyano- α - Δ^1 -cyclopenteneacetate,



This ester is prepared by the action of methyl iodide and sodium methoxide on ethyl α -cyano- Δ^1 -cyclopenteneacetate. Sodium (2 grams) was dissolved in methyl alcohol, and to the cooled solution the cyano-ester (15 grams) was added. The mixture at once assumed a deep red colour, and methyl iodide (30 grams) was then added in small quantities at intervals, care being taken to avoid any increase of temperature. After keeping for an hour, and then warming for a short time on the water-bath, the deep colour faded to yellow, and the liquid was poured

ACETIC ACID AND 1-METHYL- Δ^2 -CYCLOHEXENE-3-ACETIC ACID. 491

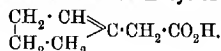
into water, acidified, and extracted with ether, washed with sodium carbonate, dried, and evaporated. The methyl-substitution product distils constantly at $160^\circ/20$ mm. as a colourless oil, with an odour resembling its lower homologue; it showed no signs of crystallising even when placed in ice:

0.1279 gave 0.3156 CO_2 and 0.0889 H_2O . $\text{C} = 67.3$; $\text{H} = 7.7$.

$\text{C}_{10}\text{H}_{18}\text{O}_2\text{N}$ requires $\text{C} = 67.0$; $\text{H} = 7.3$ per cent.

Hydrolysis.—The hydrolysis was effected by means of methyl-alcoholic potash, and the resulting cyano-acid was submitted to distillation under diminished pressure, when carbon dioxide was eliminated, and a nitrile, possessing an odour quite distinct from that of the lower homologue (see below), passed over at $123^\circ/50$ mm. The analysis gave numbers which were approximately correct for α - Δ^1 -cyclopentenepropionitrile.

Δ^1 -cyclopenteneacetonitrile and Δ^1 -cyclopenteneacetic Acid,



When α -cyano- Δ^1 -cyclopenteneacetic acid is distilled under 100 mm. pressure, it suffers decomposition with elimination of carbon dioxide and formation of Δ^1 -cyclopenteneacetonitrile. On refractionating the distillate, it was readily obtained pure as a colourless oil, possessing a pungent odour characteristic of a nitrile, and distilling at $124^\circ/100$ mm. or $150^\circ/200$ mm.:

0.1080 gave 12.4 c.c. N_2 at 20° and 758 mm. $\text{N} = 13.1$.

$\text{C}_7\text{H}_9\text{N}$ requires $\text{N} = 13.1$ per cent.

The hydrolysis of this nitrile was effected by digesting it for twenty-four hours with 20 per cent. alcoholic sulphuric acid, and, on cooling, ammonium sulphate separated in crystals. After dilution with water, the product was extracted with ether, the ethereal solution washed with water until free from alcohol, and then with dilute sodium carbonate; the residue obtained after evaporation of the ether consists of a mixture of ethyl Δ^1 -cyclopenteneacetate with some unchanged nitrile, and this was distilled under diminished pressure. The mixture was now digested with methyl-alcoholic potash for half an hour, and, after the addition of water, the nitrile was removed by extraction with ether. The alkaline solution was evaporated, and, when cool, acidified with dilute hydrochloric acid. An oily acid was precipitated, which soon solidified, and, after remaining in contact with porous porcelain, it was purified by distillation under diminished pressure and analysed immediately:

0.1220 gave 0.2968 CO_2 and 0.0859 H_2O . $\text{C} = 66.4$; $\text{H} = 7.8$.

$\text{C}_7\text{H}_{10}\text{O}_2$ requires $\text{C} = 66.7$; $\text{H} = 7.9$ per cent.

An analysis of the *silver salt* gave the following result:

0.1440 gave 0.0660 Ag. Ag = 45.9.

$C_7H_9O_2Ag$ requires Ag = 46.3 per cent.

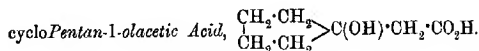
Δ^1 -cyclopenteneacetic acid crystallises in colourless prisms, melting, as found by Wallach, at 51–52°, and distils as a viscid oil at 132°/16 mm. (Wallach: 122°/11 mm.). It is readily soluble in most organic solvents. After exposure to the air, it gives numbers on analysis which are always low in carbon; this is due to oxidation at the double linking, which takes place with greater ease than in the case of the six-carbon-ring homologue (Trans., 1908, 93, 1960), and from the point of view of comparative stability this observation is of considerable interest.

1:2-Dibromocyclopentene-1-acetic acid melts at 87–88° (compare Wallach and Speransky, *Annalen*, 1902, 323, 159).

1-Bromocyclopenteneacetic acid was obtained by stirring the solid unsaturated acid with aqueous hydrobromic acid saturated at 0°. The product was poured on porous porcelain, and afterwards recrystallised from light petroleum, from which solvent it separates in thin, colourless plates, melting at 76°:

0.1770 gave 0.1625 AgBr. Br = 39.0.

$C_7H_{11}O_2Br$ requires Br = 38.7 per cent.



Ethyl cyclopentan-1-olacetate, prepared as described by Wallach and Speransky (*Annalen*, 1902, 323, 159), was obtained as a viscid, colourless oil, distilling at 128–130°/20 mm. (Wallach and Speransky give 105–107°/11 mm.). This ester was hydrolysed with methyl-alcoholic potash, and the hydroxy-acid extracted from the acidified solution by means of ether. On evaporation of the dried ethereal solution, the acid solidified, and was obtained pure by recrystallisation from a mixture of benzene and light petroleum, when it separated in colourless plates containing $\frac{1}{2}H_2O$, and melted at 76°. This acid is very soluble in benzene, ethyl acetate, chloroform, or alcohol, but sparingly so in light petroleum or water:

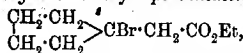
0.1176 gave 0.2370 CO_2 and 0.0920 H_2O . C = 54.9; H = 8.7.

$C_7H_{12}O_3 \cdot \frac{1}{2}H_2O$ requires C = 54.9; H = 8.5 per cent.

The *silver salt* was obtained in flat needles:

0.1960 gave 0.0840 Ag. Ag = 42.8.

$C_7H_{11}O_3Ag$ requires Ag = 43.0 per cent.

Ethyl 1-Bromocyclopentaneacetate,*and Ethyl Δ^1 -cyclopenteneacetate.*

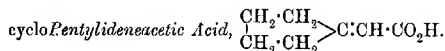
When ethyl cyclopentan-1-olacetate is gently warmed in contact with a saturated solution of hydrobromic acid, the bromo-ester is formed, and if the product is left not longer than twenty minutes in contact with the aqueous solution, it escapes hydrolysis to the corresponding acid. The heavy oil which is formed on the addition of water is extracted with ether, washed with water and sodium carbonate, and then dried and distilled, when *ethyl 1-bromocyclopentaneacetate* is obtained as a pleasant smelling, colourless oil, which distils at $142-143^\circ/35$ mm.

Hydrobromic acid is readily eliminated from the above bromo-ester, and in the present case the process was carried out by digesting for two hours with twice its volume of dimethylaniline. On adding water and acidifying with dilute hydrochloric acid, the base was recovered at the end of the operation, and the resulting unsaturated ester extracted with ether and purified by distillation, when it was obtained as a colourless oil distilling at $101^\circ/16$ mm. This was analysed immediately, with the following result:

0.1375 gave 0.3550 CO_2 and 0.1111 H_2O . C = 70.4; H = 9.0.

$\text{C}_9\text{H}_{14}\text{O}_2$ requires C = 70.1; H = 9.1 per cent.

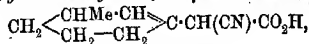
This ester on hydrolysis gave the corresponding Δ^1 -cyclopentene-acetic acid, m. p. $51-52^\circ$, which has already been described on p. 492.



In order to prepare this acid, cyclopentan-1-olacetic acid (6 grams) (see p. 492) was digested for two hours with acetic anhydride (8 grams), and at the end of this time the product was distilled in current of steam and a large volume of distillate collected (Wallach, *Annalen*, 1909, 365, 255). The distillate was saturated with ammonium sulphate and extracted with ether, the ethereal solution washed many times with water to remove acetic acid, and then dried and evaporated. The residue soon crystallised in long, slender needles, which melted at 61° . The acid decolorises cold permanganate solution instantly, with the formation of cyclopentanone. The silver salt prepared in the usual way was analysed:

0.2170 gave 0.1007 Ag. Ag = 46.4.

$\text{C}_7\text{H}_9\text{O}_2\text{Ag}$ requires Ag = 46.3 per cent.

α -Cyano-1-methyl- Δ^2 -cyclohexene-3-acetic Acid.*and its Ethyl Ester.*

When 1-methylcyclohexan-3-one is mixed in alcoholic solution with the sodium derivative of ethyl cyanoacetate in equimolecular quantities, condensation takes place in a similar manner to that described in the case of cyclopentanone on p. 489 if the same conditions are observed. The product was diluted, acidified, extracted with ether, and washed with water and dilute sodium carbonate (4). The residue from the ethereal solution yielded a little unchanged 1-methylcyclohexan-3-one on distillation under diminished pressure, also a small quantity of 1-methyl- Δ^2 -cyclohexene-3-acetonitrile (see p. 495), and then ethyl α -cyano-1-methyl- Δ^2 -cyclohexene-3-acetate distilled over at 168–169°/18 mm. as a colourless oil, possessing a faint but characteristic odour:

0.1459 gave 0.3720 CO_2 and 0.1074 H_2O . C = 69.5; H = 8.2.

0.1588 „ 9.6 c.c. N_2 at 9° and 744 mm. N = 7.1.

$\text{C}_{15}\text{H}_{17}\text{O}_2\text{N}$ requires C = 69.6; H = 8.2; N = 6.7 per cent.

This ester can also be obtained in a better yield by employing equimolecular quantities of 1-methylcyclohexan-3-one and ethyl cyanoacetate and adding a few drops of piperidine. Under the influence of this reagent, the condensation is complete in about two hours, and the mixture soon becomes turbid, owing to the separation of water. Towards the end of the operation the mixture was heated in a rapidly boiling-water bath. The resulting yellow oil was diluted with water, extracted with ether, washed well with dilute hydrochloric acid, dried, and distilled. The yield is about 60 per cent.

The cyano-acid is obtained in excellent yield from the sodium carbonate washings (4) in the first condensation. The alkaline solution was acidified with dilute hydrochloric acid and extracted with ether, and the ethereal solution dried and evaporated. The residue consisted of a viscid, yellow oil, which was cooled in a freezing mixture, when it soon solidified. The solid was freed from adhering oil by placing it in contact with porous porcelain, and afterwards recrystallised from benzene, from which it separates in short needles, melting sharply at 112°:

0.1122 gave 0.2738 CO_2 and 0.0722 H_2O . C = 66.9; H = 7.1.

0.1558 „ 10.9 c.c. N_2 at 21° and 760 mm. N = 7.9.

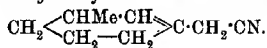
$\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}$ requires C = 67.0; H = 7.2; N = 7.8 per cent.

α -Cyano-1-methyl- Δ^2 -cyclohexene-3-acetic acid is insoluble in cold, and slightly soluble in warm, water; it is also insoluble in light

ACETIC ACID AND 1-METHYL- Δ^2 -CYCLOHEXENE-3-ACETIC ACID. 495

petroleum, but dissolves with considerable readiness in alcohol, benzene, or ethyl acetate. In contact with concentrated alkali in the cold it is decomposed, with formation of 1-methylcyclohexan-3-one. It does not react with hydrobromic acid to form an additive product.

1-Methyl- Δ^2 -cyclohexene-3-acetonitrile,



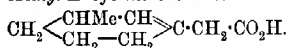
This nitrile is prepared by the slow distillation of α -cyano-1-methyl- Δ^2 -cyclohexeneacetic acid under a pressure of 90 mm. The operation is accompanied by the elimination of carbon dioxide, and the nitrile passes over as a light mobile liquid between 150° and 160°. It was purified by redistillation, when it boiled constantly at 152°/90 mm. (Wallach and Beschke, *Annalen*, 1906, 347, 341, give 108—112°/10 mm. and 230—234° under atmospheric pressure), and was obtained as a colourless oil, possessing a powerful nitrile-like odour:

0.1473 gave 0.4300 CO₂ and 0.1276 H₂O. C = 79.6; H = 9.6.

0.1141 „ 10.4 c.c. N₂ at 20° and 758 mm. N = 10.4.

C₉H₁₃N requires C = 80.0; H = 9.6; N = 10.3 per cent.

1-Methyl- Δ^2 -cyclohexene-3-acetic Acid,



The hydrolysis of the above-mentioned nitrile was carried out under the following conditions:

The pure nitrile, boiling constantly at 152°/90 mm., and prepared from recrystallised cyano-acid, m. p. 112°, was digested for twelve hours with 10 per cent. alcoholic sulphuric acid. The mixture on cooling was poured into water, the precipitated oil extracted with ether, and the ethereal solution dried and evaporated. The residue consisted of ethyl 1-methyl- Δ^2 -cyclohexene-3-acetate, along with some unchanged nitrile, and this mixture was distilled under 100 mm. pressure and then warmed for fifteen minutes with methyl-alcoholic potash. The product was diluted with water, and the nitrile removed by extraction with ether. The aqueous solution was evaporated gently, and then acidified, when the acid separated as an oil, which was dissolved in ether and afterwards distilled. It boiled at 152—158°/20 mm., but was still further purified by solution in ether, extracting by means of sodium carbonate, and again recovering from the alkaline solution. It now distilled constantly at 149°/14 mm., and when cooled in ice rapidly solidified to a mass of fern-shaped crystals. These were drained on an ice-cold porous tile, and the adhering oil was absorbed, leaving the acid as lustrous crystals, which melted about 25°.

Both in odour and appearance this substance closely resembles 1-methyl- Δ^2 -cyclohexene-1-acetic acid, m. p. 41° , obtained by Marchwald and Meth (see introduction), and Δ^1 -cyclohexeneacetic acid, m. p. 38° :

0.1520 gave 0.3879 CO_2 and 0.1270 H_2O . C = 69.6; H = 9.2.

$\text{C}_9\text{H}_{14}\text{O}_2$ requires C = 70.1; H = 9.1 per cent.

Its basicity was determined by titrating with $N/10$ -sodium hydroxide:

0.2658 neutralised 0.0696 NaOH, whereas the same weight of a monobasic acid, $\text{C}_9\text{H}_{14}\text{O}_2$, requires 0.0690 NaOH.

It is exceedingly probable that the above acid, m. p. 25° , is identical with the oily acid previously obtained by Wallach and Salkind (*Annalen*, 1900, 314, 151; compare also Tétay, *Bull. Soc. chim.*, 1902 [iii], 27, 598, and Wallach and Beschke, *Annalen*, 1906, 347, 340).

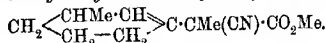
The amide of this acid was prepared by digesting 1-methyl- Δ^2 -cyclohexene-3-acetonitrile with alkali. It crystallises from ether in glistening, silvery plates, melting at 150° . Wallach and Beschke (*Annalen*, 1906, 347, 340) give the melting point of this amide as $153\text{--}154^\circ$:

0.1395 gave 11.2 c.c. N_2 at 14° and 760 mm. N = 9.4.

$\text{C}_9\text{H}_{13}\text{ON}$ requires N = 9.1 per cent.

Methylation of Ethyl α -Cyano-1-methyl- Δ^2 -cyclohexene-3-acetate.

Formation of Methyl α -Cyano- α -1-methyl- Δ^2 -cyclohexene-2-propionate,



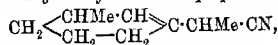
Ethyl- α -cyano-1-methyl- Δ^2 -cyclohexene-3-acetate was mixed in methyl-alcoholic solution with an equimolecular quantity of sodium methoxide, and an excess of methyl iodide was gradually added. The reaction was vigorous, and required cooling at intervals; it was completed by warming gently on the water-bath for fifteen minutes. The product was poured into water, extracted with ether, and distilled, when it passed over constantly at $140\text{--}142^\circ/10$ mm.:

0.1299 gave 0.3298 CO_2 and 0.0945 H_2O . C = 69.3; H = 8.1.

0.1900 „ 11.9 c.c. N_2 at 18° and 760 mm. N = 7.2.

$\text{C}_{12}\text{H}_{17}\text{O}_2\text{N}$ requires C = 69.6; H = 8.2; N = 6.7 per cent.

α -1-Methyl- Δ^2 -cyclohexene-3-propionitrile,



and α -1-Methyl- Δ^2 -cyclohexene-3-propionic Acid.

The above cyano-ester was hydrolysed by boiling for ten minutes with methyl-alcoholic potash, and, after the addition of water and

evaporating, the alkaline solution was acidified and the oil which separated was extracted with ether. The cyano-acid could not be obtained crystalline, and therefore the crude oil was distilled under 90 mm. pressure, when carbon dioxide was eliminated and an excellent yield of nitrile was obtained. It was purified by redistillation, and was obtained as a colourless, mobile liquid, possessing a pleasant sweet odour, and boiling at 152–153°/90 mm.:

0.1382 gave 10.4 c.c. N_2 at 17° and 757 mm. $N = 9.6$.

$C_{10}H_{15}N$ requires $N = 9.4$ per cent.

Hydrolysis.—The nitrile was boiled for twenty-four hours with twice its volume of alcohol, containing 20 per cent. of sulphuric acid. It was observed that the reaction proceeded very slowly, in striking contrast to the hydrolysis of the lower homologue, 1-methylcyclohexene-3-acetonitrile (p. 495). The product was diluted with water, extracted with ether, and the mixture of nitrile and ester distilled under 100 mm. pressure. The distilled oil was now digested for ten minutes with methyl-alcoholic potash, and, after dilution with water, the nitrile was removed by extraction with ether; on acidifying the alkaline solution the acid was obtained, and was distilled under 12 mm. pressure, when it passed over as a colourless oil, boiling at 144–148° and possessing the odour of a fatty acid:

0.1195 gave 0.3110 CO_2 and 0.0999 H_2O . $C = 71.1$; $H = 9.3$

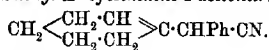
$C_{10}H_{16}O_2$ requires $C = 71.4$; $H = 9.5$ per cent.

Its basicity was controlled by titrating with $N/10$ -sodium hydroxide:

0.2146 neutralised 0.0508 $NaOH$, whereas the same weight of a monobasic acid, $C_{10}H_{16}O_2$, requires 0.0511 $NaOH$.

The above acid is doubtless identical with that obtained by Wallach and Evans (*Annalen*, 1908, 360, 51), who give the boiling point 155–157°/17 mm.

α -Phenyl- Δ^1 -cyclohexene-1-acetonitrile,



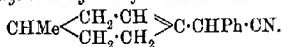
This substance was prepared as follows: Phenylacetonitrile (12 grams) was mixed with a solution of sodium (2.3 grams) in ethyl alcohol, and, after cooling, cyclohexanone (10 grams) was added. The product was heated for fifteen minutes on the water-bath, and the solution became somewhat yellow in colour. It was then cooled, diluted with water, acidified, and the precipitated oil extracted with ether. The ethereal solution was washed with water and dilute sodium carbonate, dried, and evaporated. On distillation of the residue, a colourless oil was obtained, which distilled at 176°/10 mm., and possessed a pleasant ethereal odour:

0.1160 gave 0.3618 CO_2 and 0.0825 H_2O . $\text{C} = 85.1$; $\text{H} = 7.9$.
 $\text{C}_{14}\text{H}_{15}\text{N}$ requires $\text{C} = 85.3$; $\text{H} = 7.6$ per cent.

A portion of the distillate, which was too small to investigate, crystallised after some time.

The hydrolysis of this nitrile was attempted with alcoholic sulphuric acid, and also with alkalis, but the result in each case was the decomposition of the molecule with the formation of phenylacetic acid and cyclohexanone.

α -Phenyl-1-methyl- Δ^3 -cyclohexene-4-acetonitrile,



The preparation of this nitrile is analogous to that which has been described above. The oil on distillation passed over as a colourless liquid at $191^\circ/13$ mm., and possessed a faint but pleasant odour of nitrile:

0.1133 gave 0.3533 CO_2 and 0.0849 H_2O . $\text{C} = 85.0$; $\text{H} = 8.3$.

0.1263 „ 7.6 c.c. N_2 at 18° and 752 mm. $\text{N} = 6.8$.

$\text{C}_{15}\text{H}_{17}\text{N}$ requires $\text{C} = 85.3$; $\text{H} = 8.1$; $\text{N} = 6.6$ per cent.

We wish to extend our thanks to Prof. W. H. Perkin for the interest he has manifested in the progress of this investigation.

THE UNIVERSITY,
 MANCHESTER.

LIV.—*The Direct Union of Carbon and Hydrogen at High Temperatures. Part II.*

By JOHN NORMAN PRING.

THE question of the direct union of carbon and hydrogen, which formed the subject of a previous paper by the author in conjunction with R. S. Hutton (Trans., 1906, **89**, 1591), has recently received a good deal of attention. In the paper just cited, the synthesis of acetylene at relatively very low temperatures (from 1850° upwards) was established, but the investigation of the formation of methane at lower temperatures gave less decisive results, and all that could be said was that the reactivity of the carbon diminished with continued use, and that the presence of impurities increased the methane formation, probably by catalysis.

As the temperature was raised in approaching the acetylene stage, and above this temperature, an increase in the methane was observed, which may be explained by the decomposition of the acetylene and the well-known greater stability of methane.

The present work is intended, by still greater precaution in the purification of the reacting substances, and by approaching the equilibrium stage from the opposite side, to clear up some of the outstanding points of uncertainty, and particularly to ascertain the equilibrium values of methane in the system methane, hydrogen, and carbon over a large range of temperatures.

Bone and Jerdan (*Trans.*, 1897, **71**, 41; 1901, **79**, 1042) first announced the possibility of obtaining methane by the direct union of carbon and hydrogen at 1200°. The percentage of methane obtained in these experiments varied from 0.7 to 1.4, mean 1.26.

Berthelot (*Ann. Chim. Phys.*, 1905, [viii], **6**, 183) disputed the above results, and emphatically expressed his belief that no hydrocarbons are produced at 1200–1350°, provided that the reacting materials are subjected to an exhaustive purification.

Mayer and Altmayer (*Ber.*, 1907, **40**, 2134) investigated the methane equilibrium in the system methane, hydrogen, and carbon. Hydrogen was allowed to react with carbon, to which nickel was added to serve as a catalyst. Experiments on the direct formation and on the decomposition of methane were made between the temperatures 470° and 620°.

In the thermodynamical equation:

$$KT = -18507 + 5.9934 T \log T + 0.002936 T^2 + RT \log \frac{\text{CH}_4}{(\text{H}_2)^2}$$

as expressed by Haber, which gives the equilibrium ratio of methane to hydrogen at all temperatures, the constant K was found by Mayer and Altmayer to be 21.1. At 1200° (1473° abs.) this gives the value of 0.07 per cent. for methane.

The experimental work is not, however, at all conclusive, as analyses of the gases show amounts of nitrogen varying from 2 to 20 per cent., and the percentages of carbon monoxide are not published.

H. von Wartenberg (*Zeitsch. anorg. Chem.*, 1909, **52**, 299) investigated the cyanogen, hydrocyanic acid, and acetylene equilibria, but his experiments were carried out in a very rough manner, and he only extended the work to exceedingly low concentrations of acetylene. In criticising the work of the present author and Hutton, Wartenberg overlooks the fact of the decomposition of acetylene into methane, and points out the anomaly of acetylene which is endothermic and methane which is exothermic both increasing in quantity at the higher temperatures.

Bone and Coward (Trans., 1908, 93, 1975) extended the earlier work of Bone and Jerdan, and claimed finally to have proved the direct union of carbon and hydrogen by the conversion of given weights of carbon into a practically quantitative yield of methane. Although it seems probable that the conclusions of Bone and Jerdan and Bone and Coward, that carbon unites directly with hydrogen to form methane, will be upheld, the fact that in their experiments the carbon was always in contact either with some known catalyst or with porcelain, which, by reduction, might yield a catalytically active compound, fully justifies the further investigation of this reaction, which, moreover, is essential before concluding that direct union occurs.

For these reasons it was thought desirable, in the course of the present investigation, to adopt means to carry out the purification of the carbon to the highest possible degree, and to use hydrogen in the purest and driest condition, so as to eliminate any possible complication through the presence of carbon monoxide and nitrogen. It was also thought it would be of interest to investigate different kinds of carbon in their behaviour towards hydrogen. The varieties studied were retort carbon, sugar-charcoal, and graphite.

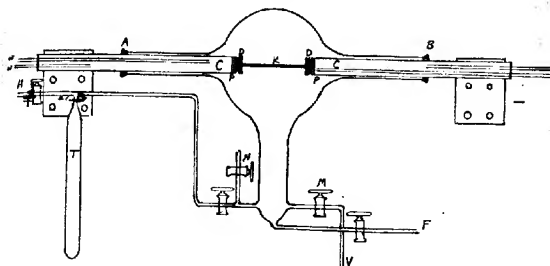
The method employed was similar to that used in the earlier work (Pring and Hutton, *loc. cit.*), and consisted in the use of rods of carbon, or of a graphite tube provided with a narrow slit along the top, and inside which could be placed the variety of carbon it was desired to study. These rods or tubes, which could be heated to any desired temperature by the passage of an electric current, were suitably mounted at a considerable distance from the glass walls of the containing vessel, and all contact of the heated parts of the carbon with any substance but the surrounding hydrogen was avoided.

The temperature of the carbon rods, in this manner, is surprisingly uniform, and can be readily estimated by means of a Wanner optical pyrometer.

A tubular glass flask, of $2\frac{1}{2}$ litres capacity, formed the reaction vessel, as shown in Fig. 1. The tubes *CC*, of brass or copper, were stopped at *PP* with brass plugs by brazing. Graphite pieces *DL* were inserted by mere contact in holes bored in the brass plugs and the graphite supported the carbon rod or graphite tube *K*. A slow circulation of water through the metal tubes by means of the tubes *vw* during the heating of the rods sufficed to keep the former quite cold. No visible heating of the graphite end pieces was ever observed, whilst the temperature of the rod was uniform to within 2 or 3 mm. from these supports. The metal tubes were fitted gas-tight at *A* and *B* by soft wax, which was occasionally

coated over with a solution of collodion in alcohol. These wax linings allow the tubes a little play during the expansion of the rod by heat and remain perfectly gas-tight under these conditions, even when the flask is completely evacuated. The leak of air into the vessel seldom corresponded with more than 1 mm. when the flask was kept for one day under 1 cm. pressure. A charcoal tube was fitted at *T*, which could be cooled by liquid air, and thus complete the exhaustion of the vessel. Before each series of experiments, this exhaustion was allowed to proceed for a few hours, and the rod kept at a temperature of about 1500° in order to dry the inside walls of the vessel as completely as possible and remove any occluded gas or final impurity from the carbon. The outlet tube *H* was to enable

FIG. 1.



Scale : cms.

preliminary partial exhaustion of the apparatus by a water pump and the outlet *K* led to a mercury gauge and to a Töpler mercury pump, where a more complete exhaustion could be effected or samples of gas withdrawn from the vessel for analysis. The hydrogen used in these experiments was generated by the electrolysis of baryta solution. The baryta was for this purpose recrystallised several times, and the electrolysis conducted in a large U-tube placed in a hot-water bath, a current of about 3 amperes being used. The hydrogen was then passed through a heated Jena combustion tube filled with copper gauze, a small heated tube filled with platinised asbestos, and then through a calcium chloride tube. Two methods were then at different times used for further purification of the gas.

A. After leaving the calcium chloride tube, the hydrogen was

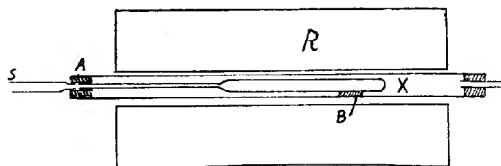
passed through a spiral glass tube, cooled on the outside by liquid air. The air in the drying tubes was first displaced by passing a current of hydrogen through for several hours, and allowing to escape through a side-tube, which dipped under mercury. The hydrogen was then admitted through the tap *M*, which could be carefully regulated, into the vacuous globe.

B. The gas was filtered through a specially constructed palladium tube, making use of the well-known permeability of this metal to hydrogen when slightly heated.

The tube was of the form shown in Fig. 2 at *X*, the total length being 30.5 cm., external diameter of wide part 5 mm., and of narrow part 2 mm., thickness of walls 0.5 mm., weight 14.2 grams. The tube was connected to the glass at *A* by means of rubber valve tubing, which was then covered with pressure tubing.

The palladium was encased in a Jena glass tube, actual contact with the glass being avoided by a palladium bridge at *B*. The

FIG. 2.



glass tube was surrounded by an electrical wire resistance furnace *R*, whereby a temperature of 350–400° could be conveniently maintained. The outlet tube *S* was sealed on to the tube *V* (Fig. 1). By opening the tap *M* (Fig. 1), the palladium tube could be evacuated together with the flask, and, on warming, perfectly pure hydrogen diffused through and gradually filled the vessel. The rate of diffusion varied, of course, with the pressure inside the flask. With the palladium tube at 400°, when the vessel was vacuous, about 20 c.c., and with a pressure of 60 cm. about 5 c.c., entered per minute. It was never necessary to fill the vessel entirely, as the subsequent heating of the rod expanded the gas to atmosphere pressure.

Temperature Readings.

It was found by comparison with a thermo-element (H. C. Greenwood, *Trans.*, 1908, **93**, 1486; *Proc. Roy. Soc.*, 1909, **82**, A, 402) that the particular pyrometer used is accurate within 20° at 1250° when sighted on to the outside of the carbon rod, and that at

1550°, 1670°, and 2000° there is not a departure of more than 15° for "black body" radiation. Consequently, the only error of any magnitude which could arise at these temperatures would be due to departure from "black body" radiation, and this deviation in the case of carbon is known to be small. In the experiments described below, the pyrometer was calibrated against a thermoelement at 1200°, and then frequently checked by means of an amyl acetate lamp.

Analysis of Gas.

The estimation of the small quantities of methane in the previous work (Pring and Hutton, *loc. cit.*), which was effected in a Sodeau apparatus, without a preliminary condensation of the hydrogen, was a matter of some difficulty on account of the tendency to form oxides of nitrogen on exploding the gas with excess of oxygen.

The presence of acetylene was ascertained qualitatively by the formation of cuprous acetylide, but in the quantitative estimation, by the use of bromine or fuming sulphuric acid, no means were adopted to distinguish between the acetylene and ethylene or any other unsaturated hydrocarbon.

In the work now described, a condensation of the hydrogen was usually first made by means of palladium foil in cases where no unsaturated hydrocarbons were present. In this way, 1000 to 1500 c.c. of the resulting gases were condensed to 50—100 c.c., and thus an accuracy of from ten- to thirty-fold in the methane estimation was obtained. Samples of gas which contained unsaturated hydrocarbons, in addition to methane, were not condensed by palladium, but were analysed as follows: The gas was first treated with a solution of ammoniacal silver chloride to remove acetylene. Two separate lots of this reagent were used, the last being freshly prepared, to ensure complete removal of this gas. A treatment with bromine or fuming sulphuric acid, followed by potassium hydroxide solution, was then carried out, to remove ethylene. The carbon monoxide was then removed by two treatments with ammoniacal cuprous chloride solution, and the methane estimated by exploding with an excess of oxygen and measuring the carbon dioxide.

Purification of Carbon.

The method employed by Bone and Jerdan and Bone and Coward (*loc. cit.*) for purifying the carbon consisted in igniting the finely divided substance for several days in a stream of chlorine, followed by hydrogen, at a temperature of 1100—1200°. The disadvantage

of this method lies in the improbability of ever being able to remove the last traces of combined hydrogen, and the serious contamination which must result from contact with the containing vessel during the long period necessary for the treatment.

The methods adopted in the present investigation were as follows.

A. In the cases where amorphous carbon rods, usually of 0.4 cm. diameter and 10 cm. long (retort carbon), were used, these were placed in a carbon tube furnace and treated for two to three hours with a current of chlorine at about 1500°, and then for about fifteen minutes with a current of nitrogen, and finally for two to three hours with a current of hydrogen. The carbon tube used for this furnace was 28 cm. long and 2 cm. external diameter. Electrical connexions were made at the end by graphite rectangular bars, and a current of 160 amperes at 11 volts was found to produce a temperature of about 1550° when charcoal was used as packing around the tube.

An analysis made of a rod after this purification showed the presence of less than 0.10 per cent. of hydrogen and 0.05 per cent. of ash. After this treatment, the rod was mounted in the glass reaction vessel, being supported by the graphite end-pieces. It was here raised to a temperature of about 1500° by the passage of an electric current while the vessel was kept at a high vacuum by means of charcoal cooled by liquid air. In some experiments a measurement was made, by means of a McLeod gauge, of the pressure inside the vessel under these conditions, and was found to vary from 0.01 to 0.10 mm. It was found possible to maintain this low pressure for an indefinite period. The carbon rod, which was heated for an interval of from one to five hours, received in this way a further purification, while an effective drying of the inside of the vessel was at the same time ensured.

In addition to the above treatment, great importance is attached to the fact that the same rod was used continuously throughout a large number of experiments, after each of which the heating in vacuum was again repeated for a short time, and only the pure hydrogen was allowed to enter the vessel after each evacuation.

B. In the case of experiments with sugar-charcoal, the procedure consisted in gradually igniting sugar to a bright red heat, reducing the carbon to a fine powder, placing in a graphite boat, and treating this in the carbon tube furnace alternately with chlorine, nitrogen, and hydrogen, as described above for the rods. A tube was prepared from Acheson graphite, 9.5 cm. long, 0.95 cm. external, and 0.6 cm. internal diameter, and provided with a narrow longitudinal slit. This was subjected to a prolonged purification treatment, and then filled with the purified charcoal and mounted

in the glass vessel in the manner employed with the rods. In one series of experiments the carbon used was purified with even more rigour, by repeating the alternate treatment with chlorine, nitrogen, and hydrogen, at 1550° for six times over a total period of six hours.

A disadvantage found with these tubes is that, unlike the case of the thinner carbon rods, the temperature is only uniform over a central region of about two-thirds of the tube, and from here it gradually falls off to the cooled supports. At higher temperatures, however, this uniform zone extends over a somewhat greater length.

Another inconvenience with this method is that while the temperature of the tube is being raised, the finely divided carbon shows a curious tendency to disperse and be expelled from the aperture, even when this is very small. This scattering is much more marked when the heating is done in a vacuum, and in all cases necessitates a very gradual raising of the temperature.

C. For examining the reaction with graphite, the tube employed in the above experiments was used empty, having been purified by prolonged treatment with chlorine and hydrogen.

The procedure in an experiment was as follows. After the preliminary heating of the purified carbon in the evacuated reaction vessel, pure hydrogen was admitted through the tap *M* (Fig. 1). The pressure of hydrogen could be measured by means of the mercury gauge connected to *F*, which also led to the pump *L*. The mercury gauge also served as an outlet for the gas during its expansion through the heating of the carbon. During the experiment the current employed was kept constant, and temperature readings were taken at frequent intervals by the Wanner optical pyrometer. At the end of each experiment the gas was removed by a Töpler pump and transferred to a graduated gas holder containing glycerol and water, and after measurement was condensed by palladium foil. Sixty grams of this foil, cut into small strips, were, for this purpose, placed in a 300 c.c. flask provided with a wide ground-glass stopper and a side-tube with a ground joint and mercury seal. The flask was exhausted by a Töpler pump, and the gas from the holder then allowed to enter. The flask was heated by a water-bath to 80 – 100° , when absorption of the hydrogen was very rapid if the amount of carbon monoxide present was below 0.01 per cent. The residual gas was removed by the pump, measured over mercury, and analysed.

Tabulated List of Results.

Values for the methane, given to two places of decimals, denote that the analysis has been made on the uncondensed gas, whilst

the methane in the gas condensed by palladium has been estimated to three places. The same carbon was used throughout each series without, in any way, dismantling the apparatus.

Part 1.—Reactions Examined in Presence of Carbon Monoxide.

A. Sugar-charcoal in graphite tube.

Series 1.—Sample purified by heating once in chlorine, nitrogen, and hydrogen alternately for one hour at 1550°, and then for half an hour in a vacuum, at 1200°, in the reaction vessel:

Order of experiment.	Temperature.	Time in hours.	Product (percentage).		
			CO.	CH ₄ .	N ₂ .
1	1200—1250°	2	0.70	0.29	0.15
2	1345	1½	0.66	0.247	—

Series 2.—Sample of sugar-charcoal purified by heating alternately in chlorine, nitrogen, and hydrogen six times for six hours at 1550°, and then in a vacuum for half an hour before each experiment:

Order of experiment.	Temperature.	Time in hours.	Product (percentage).		
			CO.	CH ₄ .	N ₂ .
1	1250°	1½	0.87	0.400	—
2	1250	1½	0.6	0.4	0.3
3	1250	2	0.35	0.279	—
4	1250—1300	1	0.36	0.198	—
5	1250	½	0.37	0.24	0.20
—	—	3	0.37	0.324	—
6	1500	1½	0.70	0.18	—

The above series clearly shows the diminution in the amount of methane formed after the first few times of use.

Series 3.—Sample of sugar-charcoal purified by heating five times alternately in chlorine, nitrogen, and hydrogen for five hours, and then in a vacuum as above:

Order of experiment.	Temperature.	Time in hours.	Product (percentage).	
			CO.	CH ₄ .
1	1230—1270°	1½	0.8	0.106
2	1615	1	1.8	0.143
3	1250	2	0.65	0.196

The above series was conducted with the view of ascertaining if the heating of the carbon to about 1600° would cause any marked diminution in the reactivity.

B. Experiments with graphite:

Order of experiment.	Temperature.	Time in hours.	Product (percentage).	
			CO.	CH ₄ .
1	1250°	1½	0.15	0.143
6	1250	½	0.01	0.046
5	1250	4	0.13	0.232
7	1250	4	0.25	0.252
3	1325	1½	0.18	0.170
4	1520	1½	1.3	0.172
5	1720	1½	2.0	0.248

Part 2.—Reactions Conducted with Very Low Concentrations of Carbon Monoxide.

Series 1.—Retort carbon.

Amorphous carbon rod purified by heating alternately in chlorine, nitrogen, and hydrogen for two hours at 1550°, and then in the reaction vessel in a vacuum at 1425° for two hours:

Order of experiment.	Temperature.	Time.	Product (percentage).			
			CO.	CH ₄ .	C ₂ H ₂ .	C ₂ H ₄ .
4	1100°	3½ hours	0.006	0.123	—	—
6	1100	13 "	0.012	{ 0.308 0.312	—	—
1	1150	2½ "	0.3	0.238	—	—
7	1200	50 mins.	<0.01	0.150	—	—
5	1200	5 hours	0.01	0.165	—	—
18	1200	11 "	<0.005	0.334	—	—
13	1200	22 "	0.01	0.842	—	—
2	1300	1½ "	0.15	0.160	—	—
3	1300	4 "	0.01	0.220	—	—
8	1400	2 "	0.010	0.178	—	—
9	1500	2 "	0.04	0.168	—	—
11	1600	35 mins.	0.001	0.210	—	—
10	1600	1½ hours	0.02	0.240	—	—
12	1725	1 hour	<0.002	0.354	—	—
14	1770	15 mins.	0.32	0.402	—	—
15	1830	12 "	0.15	0.530	nil	—
16	1850	1 hour	0.05	0.597	trace	—
17	1950	30 mins.	0.44	0.86	0.20	0.22
19	2055*	10 "	0.33	1.13	1.30	0.97

* Rod broke and arced for about three seconds at end.

Series 2.—Amorphous carbon rod, heated as last one.

1	1570°	1 hour	0.160	0.154	nil	nil
2	1620	30 mins.	0.087	0.181	"	"
3	2050	15 "	0.35	1.08	0.45	0.45
4*	2180	11 "	0.10	2.18	1.80	1.72

* Rod arced for about three seconds at end.

Part 3.—Decomposition of Acetylene and Methane in Presence of an Excess of Hydrogen at High Temperatures.

Experiments on the decomposition of these hydrocarbons were undertaken to attempt to decide to what extent methane might arise at the higher temperatures as a secondary action from the decomposition of acetylene, to measure its stability at these temperatures, and, if possible, to find the final equilibrium value of methane from the other side.

Acetylene was for this purpose prepared by dropping ethylene dibromide into hot alcoholic potash, washing the gas with alcohol, and collecting over water.

About 5 litres of this were condensed by liquid air and then allowed to evaporate, the middle portion being passed into a holder of about 200 c.c. over mercury. From here it could be admitted into the reaction vessel through the tap *N*, the connecting tube having first been evacuated, together with the vessel. Methane was prepared by decomposing commercial aluminium carbide with dilute hydrochloric acid, washing the gas well with ammoniacal cuprous chloride to remove acetylene and hydrogen sulphide, and then liquefying the methane, vaporising, and collecting the middle fraction.

Small percentages of acetylene or methane could in this way be admitted into the reaction vessel, which was then filled with hydrogen. An amorphous carbon rod was used. Samples of gas were withdrawn from the reaction vessel before and after each experiment. In some cases condensation with palladium was resorted to. The results are tabulated below:

Ex- periment.	Temperature.	Time.	Composition of gas.			
			CO.	CH ₄ .	C ₂ H ₂ .	C ₂ H ₄ .
1	1480°	0	—	—	0·6	—
		1 hour	0·15	0·32	nil	trace
		2 hours	0·2	0·25	„	„
		4½ „	0·25	0·25	„	„
2	1200°	0	—	—	3·50	—
		1½ hours	0·27	4·20	0·50	0·35
		5½ „	0·41	1·41	nil	0·35
		8 „	0·48	1·00	„	0·35
3	1775°	0	—	—	20·2	—
		10 mins.	0·08	5·93	5·02	1·13
		1 hour	0·09	0·77	nil	nil
4	1200°	0	—	6·00	—	—
		25 hours	0·073	4·63	—	—
5	1580° to 1620°	0	—	5·0	—	—
		2 hours	0·05	1·75	—	—
6	1200°	0	—	6·73	—	—
		2 hours	0·25	5·47	—	—

Experiment in which 5 per cent. of carbon monoxide was added, to study its effect on the decomposition of methane:

7	1200°	0	5.0	6.5	—	—
		3 hours	4.2	5.92	—	—
		6½ „	3.72	5.95	—	—

Part IV.—Amorphous Carbon Rod with a Deposit of Platinum on Surface to Assist the Reaction Catalytically.

This rod was purified in chlorine, nitrogen, and hydrogen at the same time as the previous ones, and was coated with a thin deposit of platinum by electro-deposition, and then heated in the reaction vessel in a vacuum at 1300° for half an hour. Pure hydrogen was then admitted, and the experiment conducted as usual. In the experiments in column B a small percentage of methane was admitted to find the equilibrium from the decomposition.

A.

Order of experiment.	Temperature.	Time.	Product (percentage).	
			CO.	CH ₄ .
1	about 1050°	1½ hours	0.052	0.866
2	„ 1100	6¼ „	0.007	0.690
8	„ 1200	2 „	0.011	0.540
3	about 1300	30 mins.	0.014	0.340
6	1500	45 „	nil	0.297

B.

Decomposition of methane with same rod.

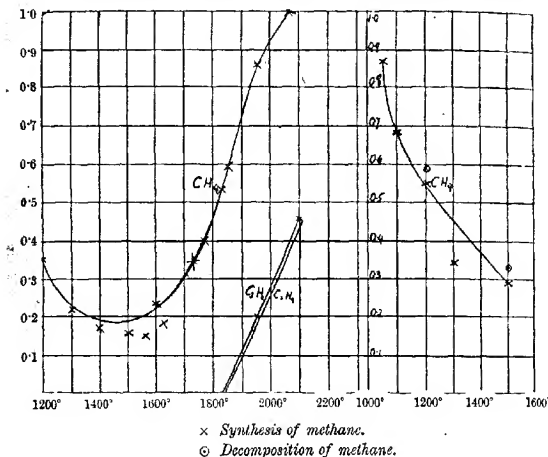
4	1175–1200°	0	—	2.31
		4 hours	0.006	1.14
5	1200	0	—	1.95
		12 „	0.003	0.594
7	1500	0	—	3.2
		2 „	1.03	0.330

Conclusions.

The experiments described above clearly show that pure carbon combines directly with pure hydrogen at all temperatures above 1100°. At 1200° the velocity of the reaction is so slow in the absence of any catalyst that the estimation of the exact equilibrium value of methane is somewhat uncertain. An experiment extending over twenty-two hours at 1200° seemed, however, to yield the limiting value of 0.35 per cent. of methane, although this could not be confirmed by approaching the equilibrium from the other side, as the decomposition of small amounts of methane by pure carbon at 1200° proceeds even more slowly than the synthetic reaction.

At 1500° an equilibrium value of 0.17 per cent. of methane appeared to be approached within about two hours, although even at this temperature the decomposition of methane was too slow to serve for the evaluation of the equilibrium quantity. More definite equilibrium values were obtained by using carbon which contained a surface deposit of platinum. In this case, in experiments at temperatures between 1050° and 1500° , the reaction was very much accelerated, and the same percentage of methane was finally obtained whether its formation or its decomposition was

Synthesis of hydrocarbons from pure amorphous carbon. Maximum amounts obtained. *Methane equilibrium with platinum coated carbon.*



nvestigated. The amount formed was 0.55 per cent. at 1200° , and 0.30 per cent. at 1500° .

Above 1550° the percentage of methane began to rise with the temperature. These increased quantities of methane do not, at these temperatures, necessarily represent equilibrium values, but probably arise from the decomposition of acetylene, although the amount of the latter gas present was too small to be detected below 1850° .

Experiments on the decomposition of hydrocarbons showed that acetylene changes quickly to methane and ethylene above 1500° , and that the methane formed is comparatively stable. This behaviour is similar to the decomposition which hydrocarbons

undergo at lower temperatures (Bone and Coward, *Trans.*, 1908, 93, 1197).

In the decomposition of acetylene at 1200—1400°, ethylene was also formed, and found to persist; consequently, this appears to preclude the possibility of the methane arising secondarily in the experiments at these temperatures, as, in these cases, no trace of ethylene was found in the gas.

Graphite and sugar-charcoal showed a similar behaviour to amorphous retort carbon in its reactivity with hydrogen.

The presence of carbon monoxide seems to have no effect on the final equilibrium in the synthesis or decomposition of methane at any temperature employed, or on the velocity of the reaction. The synthesis of acetylene could not be taken to the equilibrium stage, as with methane, in the form of apparatus used. Acetylene, being endothermic, is stable in larger amounts the higher the temperature, and would consequently undergo some decomposition in passing away from the heated carbon through the intermediate zones of temperature of the outside layers of gas.

The equilibrium values obtained in the above work probably refer to systems of different concentrations than the surrounding gases, on account of a probable condensation of gas on the surface of the carbon or catalyst. This problem is now being investigated by the use of high gaseous pressures and the examination of the effect of catalysts other than platinum.

In conclusion, I wish to express my indebtedness to Professor E. Rutherford for the facilities he has extended for conducting this research, and to Dr. R. S. Hutton for suggesting the work, and for his continued interest and assistance during its progress.

ELECTRO-CHEMICAL LABORATORY,
THE UNIVERSITY,
MANCHESTER.

LV.—*The Colour and Constitution of Azo-compounds.* *Part V.*

By JOHN THEODORE HEWITT and FERDINAND BERNARD THOLE.

DURING the progress of some work on the relationships existing between the constitution and selective absorption of certain polyazo-compounds, the authors of the present communication were much struck with the great colour change which takes place on diazotising

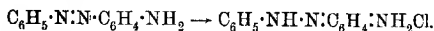
aminoazobenzene in hydrochloric acid solution. As is well known, azobenzene and aminoazobenzene both dissolve in alcohol, with a shade which is yellow in dilute solution, the head of the band of slowest oscillation, but little persistence, lying at about 2200 oscillation frequency in the case of azobenzene (Hartley, *Trans.*, 1887, 51, 152; Baly and Tuck, *Trans.*, 1906, 89, 985; Hantzsch, *Ber.*, 1909, 42, 2132), and apparently at about the same point with the amino-derivative (compare Landauer, *Ber.*, 1881, 14, 391, and C. Graebe, *Zeitsch. physikal. Chem.*, 1892, 10, 689). The best marked and most persistent band given by alcoholic solutions of azobenzene has its head at an oscillation frequency of about 3200.

Similar observations have been made in the case of dimethyl-aminoazobenzene (2430, Hantzsch, *loc. cit.*, p. 2133), *p*-aminobenzeneazophenol (2600), and *p*-dimethylaminobenzeneazophenol (2400, Hewitt and Thomas, *Trans.*, 1909, 95, 1297).

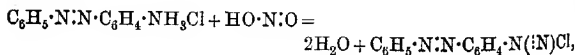
In all cases, however, where an amino-group occupies a para-position with respect to the azo-group, the formation of a monacid salt by the addition of dilute hydrochloric acid in sufficient quantity conditions a change in colour to red, the oscillation frequencies of the heads of the persistent band of longest wave-length lying at about the same point for the compounds enumerated; this is shown in the following table:

<i>p</i> -Aminoazobenzene	2000 (see Fig. 1)
<i>p</i> -Dimethylaminoazobenzene	1900 (Hantzsch)
<i>p</i> -Aminobenzeneazophenol	1800 (Hewitt and Thomas)
<i>p</i> -Dimethylaminobenzeneazophenol ...	1800 " " "

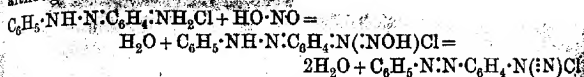
This change, which corresponds with that observed on acidifying a solution of methyl-orange, is now generally explained by supposing the hydrochlorides to be derived from the equivalent quinonoid form:



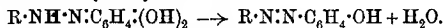
The possibility of a certain small amount of amino-aromatic salt being also present in solutions is not completely negatived, since one may adduce in support of such a proposition the fact that Hantzsch has in some cases isolated yellow salts of aminoazo-compounds, and has also obtained a tribromo-derivative of aminoazobenzene by the direct action of the halogen in glacial acetic acid solution (*Ber.*, 1908, 41, 1171, 1187, 2435); whilst, further, there is the well-known aptitude for diazotisation of the aminoazo-compounds. In the last case one is inclined to formulate the reaction as taking place according to the scheme:



althou



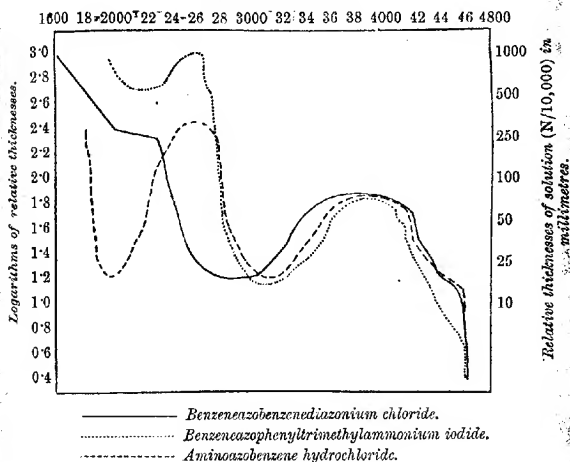
does not seem so improbable when one considers the easy way in which the quinonoid hydrates of azophenols lose water, passing directly into the hydroxyazo-form:



It is certainly highly improbable that the diazonium chlorides possess a similar structure to the salts of the parent aminoazo-

FIG. 1.

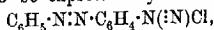
Oscillation frequencies.



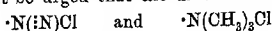
compounds, for on adding nitrite to the bluish-red solutions of the latter, the colour changes to an orange, which to the unassisted eye appears rather more red in shade than that of the free aminoazo-compounds or of azobenzene itself. In these circumstances it appeared very desirable to examine the absorption spectra, and for this purpose we have compared benzenazobenzenediazonium chloride with the hydrochloride of aminoazobenzene on the one hand, and with benzenazophenyltrimethylammonium iodide on the other. Comparison with other para-derivatives of azobenzene is also possible, and, as will be seen from the curve given in Fig. 1, benzene-

azobenzenediazonium chloride gives a curve which resembles somewhat closely that given by benzeneazophenol (Tuck, Trans., 1907, 91, 450). The head of the absorption band for benzeneazophenol lies at an oscillation frequency of about 3000, whilst for the diazonium salt examined it is about 2950. Further, both of these substances show an extension of the band towards the red end of the spectrum; a similar extension has also been observed with certain aminoazophenols by Hewitt and Thomas (*loc. cit.*).

On the same diagram will be found the curves for the absorption spectra furnished by the hydrochloride of aminoazobenzene and by benzeneazophenyltrimethylammonium iodide. The first of these substances is almost without doubt of quinonoid structure, and its absorption, which closely resembles that of the hydrochlorides of dimethylaminoazobenzene and its hydroxy- and methoxy-derivatives, is absolutely different from that of the other two compounds, which do not, however, agree as closely between themselves as might have been expected for substances possessing similar structures. It therefore remains an open question whether the constitution of the diazonium salt is to be expressed by the formula:



although it might be urged that the difference in the groups



might account for the comparatively minor differences in the absorption spectra.

Comparison of the absorption spectra of phenol (Baly and Ewbank, Trans., 1905, 87, 1351) and benzenediazonium salts would have been interesting, but since, according to Dobbie and Tinkler (Trans., 1905, 87, 273), the latter give absorption spectra similar to those of dilute solutions of the unstable diazotates, a reference to the curve given in the latter case by these authors shows that very little aid can be expected.

For the purposes of this work, aminoazobenzene was acetylated, the acetyl derivative recrystallised until of constant melting point, and hydrolysed. In examining its acid-alcoholic solution, hydrochloric acid was added in such amount as not to produce any further deepening of the red shade.

The benzeneazophenyltrimethylammonium iodide was prepared by heating benzeneazodimethylaniline with methyl alcohol and methyl iodide to 100° after keeping the mixture for eighteen hours in the cold, and reaction was already practically complete. The product was finally recrystallised from a large quantity of boiling water.

Benzeneazobenzenediazonium Chloride.—The isolation of the solid diazonium salt was effected by suspending 4.7 grams of aminoazo-

benzene hydrochloride in 150 c.c. of alcohol (96 per cent.), and adding 2.4 grams of amyl nitrite diluted with 10 c.c. alcohol. After fifteen minutes' stirring, any small solid residue was removed by filtration and the diazonium chloride precipitated by ether, collected, washed with ether, and dried over sulphuric acid. The salmon-coloured powder obtained in this way proved, under the microscope, to consist of a mass of small but well-defined prisms:

0.5506 gave 0.3211 AgCl. Cl=14.4.

$C_{12}H_9N_4Cl$ requires Cl=14.5 per cent.

The salt dissolves in alcohol and water, showing considerable stability even in alcoholic solution. The absorption spectra were observed with freshly prepared alcoholic solutions, but even after keeping overnight at the ordinary temperature a large amount of the diazonium salt was found to be still undecomposed. On heating, the salt decomposes comparatively gently; no detonation has been observed, whilst the dry salt may be kept for months without appreciable decomposition, still dissolving in water and coupling with the usual azo-components. An aqueous solution reacts, however, immediately with potassium iodide, giving *p*-iodoazobenzene.

Platinichloride.—This salt was prepared by precipitating an aqueous solution of the chloride with excess of chloroplatinic acid; after washing and drying it formed a salmon-coloured powder. This salt also shows considerable stability, and decomposes in a gentle manner when heated:

0.3228 gave 0.0768 Pt. Pt=23.8.

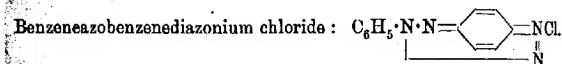
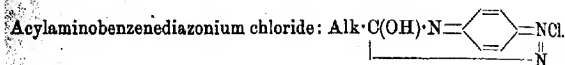
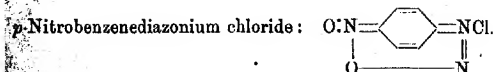
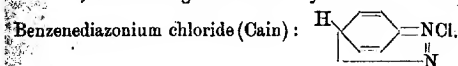
$(C_{12}H_9N_4)_2PtCl_6$ requires Pt=23.6 per cent.

No *ferrichloride* has been obtained, but solutions of the chloride yield a yellow precipitate with potassium dichromate. The salt, presumably *benzeneazobenzenediazonium dichromate*, was washed and dried, but on account of the character of the detonation which occurred on heating, an analysis was not carried out. Meldola (Trans., 1905, 87, 4) has also prepared this salt, but did not analyse it owing to its explosive properties.

The absorption spectra are not such that the authors feel justified in drawing any rigid conclusion as to the constitution of the benzeneazobenzenediazonium chloride; it is, however, a very remarkable fact that the most stable diazonium salts are always those possessing a para-substituent, especially when the latter happens to be an unsaturated and negative group. Reference may be made to the cases of *p*-nitrobenzenediazonium chloride, the acetylaminobenzenediazonium chloride described by Meldola (Proc., 1899, 15, 196; Trans., 1905, 87, 1), and to the benzenesulphonyl-

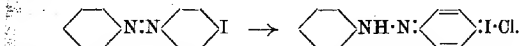
aminoaryldiazonium salts. Morgan and Alcock workers (Trans., 1905, 87, 73, 921, 1302; 1906, 88, 44, 1907, 91, 1211, 1505, 1512; 1908, 93, 602).

Morgan and Alcock (Trans., 1909, 95, 1319) adopt a modification of Cain's formula (Trans.; 1907, 91, 1040) for the constitution of diazonium salts, but apparently do not attribute the stability conferred by negative para-substituents to any essential difference in constitution. If one follows Cain in ascribing to diazonium salts a semiquinonoid structure, the possibility certainly arises that salts of the negatively substituted type may be fully quinonoid in structure, and their greater stability be thus accounted for:



Thus, whilst Cain represents the simple diazo-salts as analogues of the labile "chinols," the above representation of the negatively substituted compounds resembles the constitution attributed to the far more stable quinones.

Iodoazobenzene.—In connexion with the work described in this paper, iodoazobenzene was examined with a view to seeing if it was capable of iodonium salt formation. As amino- and hydroxy-azobenzene readily yield quinonoid salts, so it is not impossible that the iodo-derivative may give corresponding salts containing trivalent iodine:



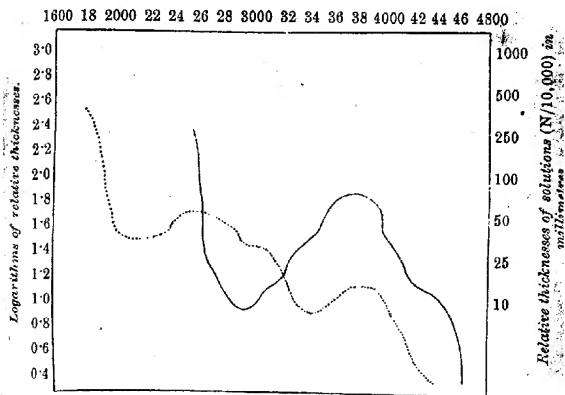
Since, however, azobenzene itself gives unstable salts with acids, it might be argued that any salts yielded by iodoazobenzene should be referred to the same type. It happens that azobenzene gives a different absorption in acid solution from that given by the mono-hydrochlorides of its amino- and hydroxy-derivatives; the absorption spectra of the two latter salts being comparable, although the head of the band of slowest frequency lies always more towards the red end of the spectrum in the case of the nitrogen compound.

When iodoazobenzene is dissolved in benzene and hydrogen

chloride, benzene and benzene combine, and separation of a certain amount of solid occurs. This method of preparing the salt, which gives such good results for hydroxyazo-compounds, is not very suitable for preparing salts of iodine derivatives, as the separation of solid matter is but slight. Nevertheless, a comparison of the absorption spectra of iodoazobenzene in alcohol alone and in alcoholic solution of hydrogen chloride (see Fig. 2) renders it quite probable that combination with hydrogen chloride occurs with formation

FIG. 2.

Oscillation frequencies.

*Iodoazobenzene in alcohol.**Iodoazobenzene in alcoholic hydrogen chloride.*

of an iodonium salt. In fact, when iodoazobenzene is moistened with benzene and exposed to gaseous hydrogen chloride, two molecules of the latter are absorbed, and a beautiful, nearly black, crystalline hydrochloride is produced.

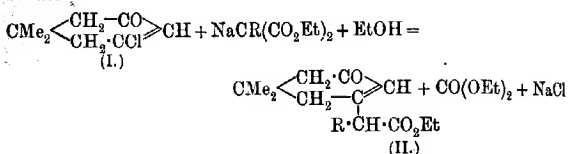
The authors acknowledge with thanks the aid afforded them by the Government Grant Committee of the Royal Society, by which the expenses of this research have been defrayed.

EAST LONDON COLLEGE.

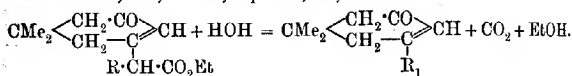
LVI.—Action of Ethyl Cyanoacetate on 5-Chloro-1:1-dimethyl- Δ^4 -cyclohexen-3-one.

By ARTHUR WILLIAM CROSSLEY and CHARLES GILLING (Salters' Fellow).

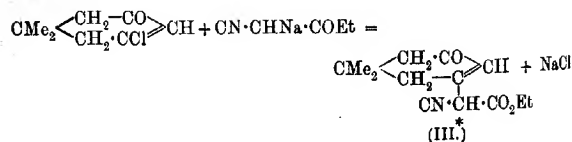
It has been previously shown (Trans., 1909, 95, 19; Proc., 1909, 25, 96) that 5-chloro-1:1-dimethyl- Δ^4 -cyclohexen-3-one (I) can be condensed with the sodium derivative of ethyl malonate (or substituted ethyl malonates) to form ethyl 1:1-dimethyl- Δ^4 -cyclohexen-3-one-5-acetate (II) with elimination of a molecule of ethyl carbonate:



These condensation products, on hydrolysis, give rise to a series of hydroaromatic ketones according to the following scheme, in which R = H, Me, or Et; R₁ = Me, Et, or Pr:



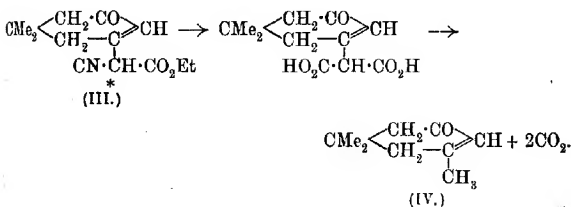
It was also mentioned (*loc. cit.*, Trans., p. 27) that a small quantity of a nitrogenous substance, melting at 141°, was always formed together with the condensation products of type II, due to the presence of ethyl cyanoacetate in the ethyl malonate employed. In continuance of the investigations on the chemical reactivity of the chlorine atom in chlorodimethylcyclohexenone, the latter substance was next condensed with the sodium derivative of ethyl cyanoacetate, when the substance melting at 141° is formed in about 75 per cent. of the theoretical quantity. It gives analytical numbers agreeing with the formula C₁₃H₁₇O₃N, and it was at first thought that the reaction should be formulated on similar lines to that taking place between ethyl malonate and chlorodimethylcyclohexenone:



This assumes that in such reactions ethyl malonate and ethyl cyanoacetate behave as if they possessed similar constitutions. The chemical properties of the condensation product are not, however, in agreement with those which a substance having formula (III) should exhibit; for whereas ethyl dimethylcyclohexenoneacetate (II) is a perfectly neutral compound containing a ketonic group, as proved by the fact that it readily forms a semicarbazone, the solution of the ethyl cyanoacetate condensation product in aqueous alcohol has well-marked acidic properties, may be titrated against standard sodium hydroxide solution, and the neutral solution so obtained gives a green colour with ferric chloride. Moreover, it can be readily esterified with ethyl alcohol containing 5 per cent. of sulphuric acid, giving rise to a mixture of two ethyl derivatives, which can be separated by fractional crystallisation, and since they both possess the same general formula, the same molecular weight, and yield the same product on hydrolysis, it seems evident that they are stereoisomeric substances.

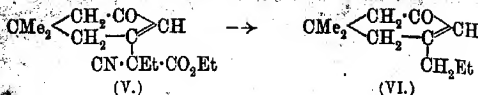
In a similar way two stereoisomeric methyl derivatives have been prepared.

The substance melting at 141° cannot be hydrolysed by long-continued boiling with an alcoholic solution of potassium hydroxide, probably on account of the stability of the potassium salt formed, but when heated for an hour with concentrated hydrochloric acid, it is converted into 1:1:3-trimethyl- Δ^4 -cyclohexen-3-one (IV), a reaction which may be provisionally represented as follows:

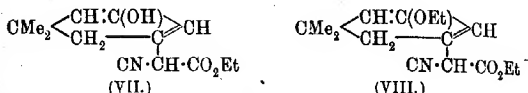


The marked acidic properties of the condensation product (III) of ethyl cyanoacetate and chlorodimethylcyclohexenone cannot be ascribed to the presence of the hydrogen atom attached to the carbon atom, marked with an asterisk, situated between the cyanogen and carbethoxyl groups. For, apart from the extreme ease with which esterification can be effected, it is found that when either of the two ethyl derivatives is boiled for an hour with concentrated hydrochloric acid, hydrolysis takes place, and trimethylcyclohexenone (IV) is produced; whereas if the constitution of the original substance is represented by formula III, the ethyl

derivative (V) would give on hydrolysis 3-propyl-1,1-dimethylcyclohexan-3-one (VI):

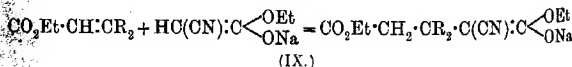


A simple explanation of the acidic properties is forthcoming if it be assumed that the original condensation product (III) undergoes tautomeric change, the ketonic oxygen becoming enolic, and giving rise to a substance of formula (VII), which on esterification (etherification) would yield (VIII).



In favour of this supposition is the fact that the substance melting at 141° forms condensation products with aniline and monomethylaniline. Whilst formula (III) admits of the formation of a compound with elimination, as water, of the ketonic oxygen with the two hydrogen atoms of the amino-group in the case of aniline, it does not admit of an analogous reaction in the case of methylaniline; but both reactions are easily explained by the adoption of formula (VII). It will be seen that the ethyl derivative (VIII) still shows the presence of a hydrogen atom attached to the carbon atom, situated between the cyanogen and carbethoxyl groups, and it should therefore be possible to introduce a second ethyl group into this position by the successive action of sodium and ethyl iodide. Although attempts were made to accomplish this end under a variety of conditions, they were always unsuccessful, and this, taken in conjunction with the fact that formula (VII) does not offer a ready explanation of the formation of two stereoisomeric modifications of the ethyl and methyl ethers, necessitates some other explanation of the reaction being sought.

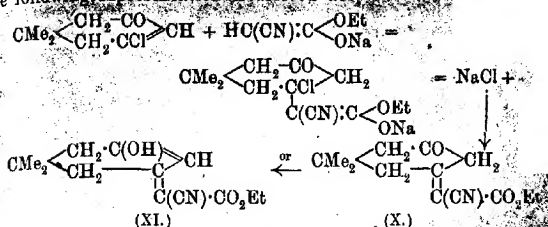
It has been proposed by J. F. Thorpe (Trans., 1900, 77, 925) that the formula which most adequately explains the behaviour of the sodium derivative of ethyl cyanoacetate is (IX), and the mechanism of its condensation with unsaturated substances is as follows:



where R may be either an alkyl group or hydrogen.

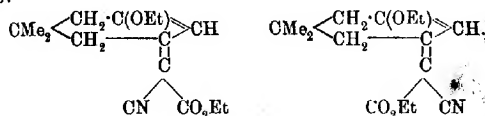
If, as kindly suggested to us by Dr. J. F. Thorpe, this formula

for ethyl cyanoacetate is obtained in the reaction under discussion, the following representation is arrived at:



and the product would be *ethyl 3-hydroxy-1:1-dimethyl-Δ⁴-cyclohexenylidene-5-cyanoacetate* (XI) (*ethyl 1:1-dimethylcyclohexan-3-onylidene-5-cyanoacetate*, X).

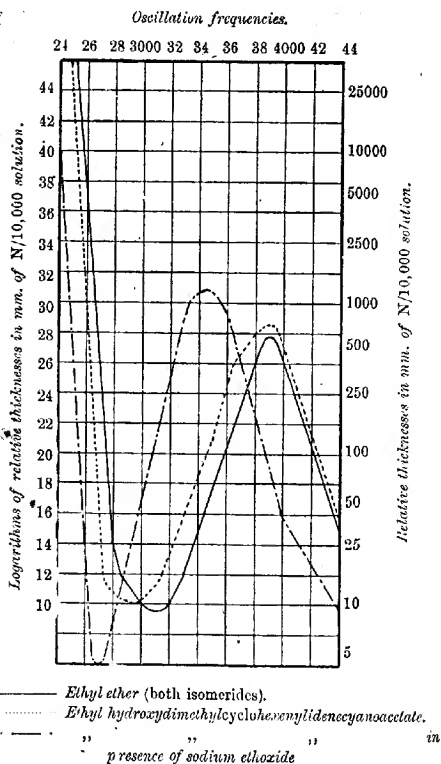
Such a formula appears to account for all the observed properties of the substance, for example, the formation of condensation products with aniline and methylaniline; its marked acidic properties, and the formation of two isomeric methyl and ethyl derivatives, which would be represented as *cis*- and *trans*-modifications:



The question naturally arises, Have the two corresponding *cis* and *trans*-forms of ethyl hydroxydimethylcyclohexenylidenecyanoacetate been observed? The answer is in the negative. This is explained by assuming that the two forms (X) and (XI) are tautomeric, and a hydrogen atom is alternating between the two positions shown, which would preclude the possibility of fixed isomerism. The introduction of an ethyl group into the molecule causes the cessation of this mobility of the hydrogen atom, and hence fixed isomerism makes its appearance. This idea corresponds with that advanced by J. F. Thorpe (*Trans.*, 1905, **87**, 1669) to account for the fact that glutacetic acid cannot be isolated in *cis*- and *trans*-modifications, whereas its dialkyl derivatives, in which the double bond becomes fixed, are capable of existing in the two forms.

We take this opportunity of expressing our cordial thanks to Mr. E. C. C. Baly and Dr. Tuck, who have examined ethyl hydroxydimethylcyclohexenylidenecyanoacetate and its two isomeric ethyl ethers spectroscopically, and who have been kind enough to make the annexed diagram and report.

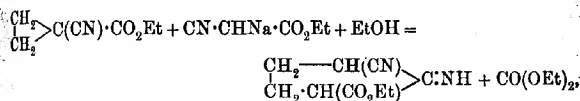
"The absorption spectra of ethyl hydroxydimethylcyclohexenylidenecyanoacetate and its two ethyl ethers were examined in alcoholic solution, and, as can be seen from the diagram, they show very persistent bands. The absorption of the two isomeric ethyl ethers is identical, and exhibits a band with its head at



$1/\lambda = 3100$. The parent substance shows a band with its head at $1/\lambda = 2950$, whilst in the presence of sodium ethoxide the band is shifted to $1/\lambda = 2700$. This shift towards the red, on the addition of alkali, is analogous to the case of dimethyldihydroresorcin, which therefore affords evidence that labile tautomerism occurs. Since the absorption band of the parent substance is nearer to the red

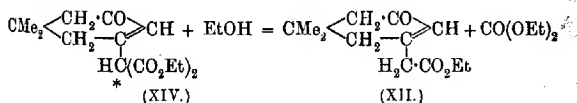
than in the case of the two ethyl ethers, the conclusion may at once be drawn that the hydrogen atom of the former is labile, which explains why the parent substance cannot be resolved into *cis*- and *trans*-modifications. That the shift in the absorption, on the addition of alkali to the parent substance, is due to the presence of labile tautomerism is proved by the fact that no change is produced by the addition of alkali to either of the ethyl ethers."

The following considerations also support the conclusion that the substance is ethyl hydroxydimethylcyclohexenylidenecyanoacetate. As already mentioned, when chlorodimethylcyclohexenone is condensed with ethyl malonate (or substituted ethyl malonates), one of the carbethoxyl groups is always eliminated as ethyl carbonate (see p. 518). Several instances of the production of the latter substance in condensation reactions have been recorded, one of the most recent being in the interaction of ethyl sodiocyanoacetate and ethyl 1-cyanocyclopropane-1-carboxylate:



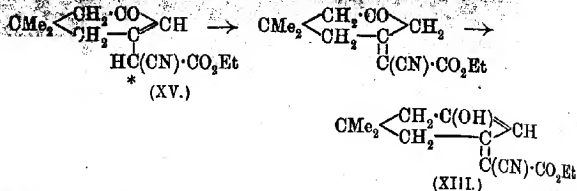
and Best and Thorpe (Trans., 1909, 95, 693) consider that the elimination of ethyl carbonate is determined, in all such cases, by spatial considerations. The present experiments lend considerable support to this view, for, in the first place, the yields of condensation products formed from chlorodimethylcyclohexenone and the substituted ethyl malonates diminished rapidly with increasing molecular weight, from which it would appear that the overcrowding in the molecule, caused by the introduction of heavier alkyl groups, renders the formation of the condensation products more and more difficult.

This affords a possible explanation of the reason for the non-acidity of ethyl dimethylcyclohexenoneacetate (XII) and the acidity of ethyl hydroxydimethylcyclohexenylidenecyanoacetate (XIII), for in the initial product of interaction (XIV) of ethyl malonate and chlorodimethylcyclohexenone, the carbon atom marked * may be regarded as overweighted and the molecule overcrowded in the region occupied by these groups, with the result that ethyl carbonate is eliminated:



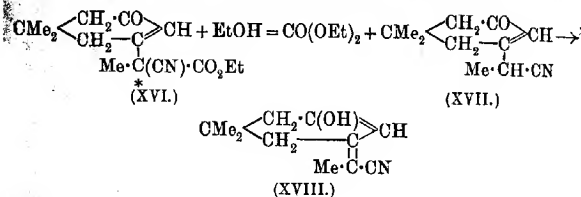
Why, then, does not a similar elimination of ethyl carbonate

take place from the condensation product (XV) formed from ethyl cyanoacetate and chlorodimethylcyclohexenone:



In this case the carbon atom marked * is not so weighted as in the substance with formula (XIV), the CN group being much lighter than a CO_2Et group, and hence the wandering of the hydrogen atom attached to this carbon atom into the ring, with formation of ethyl hydroxydimethylcyclohexenyldenecyanoacetate (XIII), sufficiently reduces the overcrowding to give a stable substance.

If, however, this hydrogen atom be replaced by a methyl group, as in the condensation of ethyl methylcyanoacetate and chlorodimethylcyclohexenone, then the carbon atom * (XVI) is again over-weighted, and as a result ethyl carbonate is eliminated:

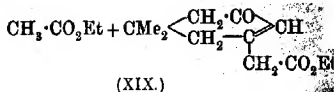
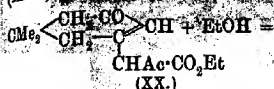


But the product so formed (XVII) is still overcrowded, and a hydrogen atom wanders into the ring, giving *hydroxydimethylcyclohexenyldenepropionitrile* (XVIII).

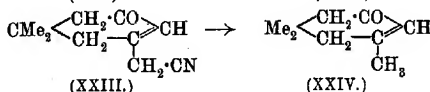
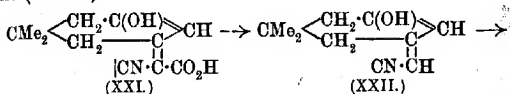
In view of these results, it seemed of interest to examine the interaction of ethyl acetoacetate and chlorodimethylcyclohexenone, when it was found that the product is the same as when using ethyl malonate, that is, ethyl dimethylcyclohexenoneacetate (XIX). Here also the initial condensation product (XX) contains the overcrowded carbon atom, marked with a *, and as a consequence the acetyl group attached to it is eliminated, by interaction with ethyl alcohol, as ethyl acetate, and a hydrogen atom takes its place.

The action of acid hydrolysing agents on ethyl hydroxydimethylcyclohexenyldenecyanoacetate can now be easily explained. The CO_2Et group (or the CN group) is first converted into CO_2H

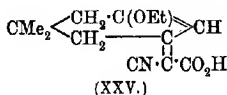
(XXI), and at once carbon dioxide is evolved, giving a substance



(XXII) which rearranges itself to dimethylcyclohexenoneacetonitrile (XXIII):



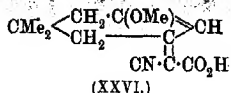
The CN group in the latter compound is then hydrolysed to CO_2H , carbon dioxide is eliminated, and trimethylcyclohexenone (XXIV) produced. The acid hydrolysis of the methyl or ethyl ethers of ethyl hydroxydimethylcyclohexenylidenecyanoacetate takes place in a similar way, but the action of alkaline hydrolysing agents on these substances is of quite a different nature. When either of the two ethyl ethers is heated with an ethyl-alcoholic solution of potassium hydroxide, the carbethoxy-group is attached, yielding ethoxydimethylcyclohexenylidenecyanoacetic acid (XXV), melting at 149° , which acid should exist in *cis*- and *trans*-forms, correspond-



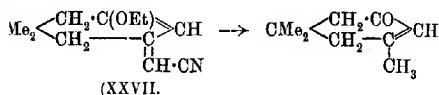
ing with the two ethyl esters. These modifications have not, however, been isolated, as no matter which of the two esters is hydrolysed, one and the same product is obtained; and it can only be concluded that, under the influence of the hydrolytic agent, the less stable form of the acid is converted into the more stable form, such cases being common among hydroaromatic substances.

When either of the methyl esters of ethyl hydroxydimethylcyclohexenylidenecyanoacetate is hydrolysed with methyl-alcoholic potassium hydroxide, methoxydimethylcyclohexenylidenecyanoacetic acid (XXVI), melting at 174° , is produced; but when the hydrolysis of the methyl ethers is carried out in ethyl-alcoholic

solution, ethoxydimethylcyclohexenylidenecyanoacetic acid (XXV), melting at 149°, is formed. The ease with which the methyl group



is replaced by ethyl is quite remarkable. An exactly similar phenomenon is observed when either form of ethoxydimethylcyclohexenylidenecyanoacetate is hydrolysed with methyl-alcoholic potassium hydroxide, the ethyl group being replaced by methyl, with production of methoxydimethylcyclohexenylidenecyanoacetic acid, melting at 174°. Such replacements of ethyl by methyl and vice versa in esters have been frequently recorded (compare Purdie, *Trans.*, 1885, 47, 855; 1887, 51, 627; 1888, 53, 391; 1891, 59, 468). When ethoxydimethylcyclohexenylidenecyanoacetic acid is heated a few degrees above its melting point, carbon dioxide is evolved, and 3-ethoxy-1:1-dimethyl-Δ²-cyclohexenylidene-5-acetonitrile (XXVII) is formed:



Although somewhat stable towards alkalis (see page 532), this nitrile is readily hydrolysed by acids, with formation of trimethylcyclohexenone.

EXPERIMENTAL.

Forty-eight grams (1 mol.) of chlorodimethylcyclohexenone were gradually added to a mixture of 70 grams (2 mols.) of ethyl cyanoacetate and 13.8 grams (2 atoms) of sodium dissolved in 170 c.c. of absolute alcohol, when a vigorous reaction at once commenced, and the liquid turned red. After heating in a water-bath for six hours, the product was poured into water and extracted four times with ether.* The aqueous alkaline liquid was then acidified with sulphuric acid, extracted four times with ether, and the ethereal solution washed, dried, and evaporated. The solid residue, weighing 51 grams after drying on porous plate, was purified by crystallisation, first from benzene, then from aqueous methyl alcohol, and analysed:

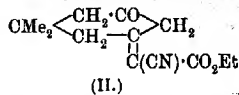
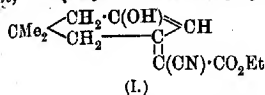
* On evaporating the ether, a residue was obtained, which was proved to consist principally of unchanged ethyl cyanoacetate and a resinous product, which yielded a solid, crystallising from methyl alcohol in fine white needles, melting at 57°, but in too small an amount for complete investigation.

0.1081 gave 0.2637 CO_2 and 0.0745 H_2O . $\text{C}=66.53$; $\text{H}=7.66$.

0.2905 gave 13.8 c.c. N_2 (moist) at 13° and 762 mm. $\text{N}=5.63$.

$\text{C}_{13}\text{H}_{17}\text{O}_3\text{N}$ requires $\text{C}=66.38$; $\text{H}=7.23$; $\text{N}=5.95$ per cent.

Ethyl 3-hydroxy-1:1-dimethyl- Δ^3 -cyclohexenyldene-5-cyanoacetate, I (ethyl 1:1-dimethylcyclohexan-3-onylidene-5-cyanoacetate,



II), is easily soluble in the cold in acetone, chloroform, alcohol, or ethyl acetate, and crystallises from benzene or aqueous methyl alcohol in fine white, glistening needles, melting at 141° . It gives with ferric chloride in alcoholic solution a fine emerald-green colour, slowly fading to olive-green, a process which is hastened by warming, and with ferric chloride in neutral solution it forms a dark green precipitate. It has a marked acid reaction in aqueous solution, and can be titrated with potassium hydroxide solution, when it behaves as a monobasic acid:

0.2412 required 10.4 c.c. $\text{N}/10\text{-KOH}$. Calculated, 10.3 c.c.

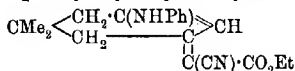
Found, $\text{M.W.}=232$. $\text{C}_{13}\text{H}_{17}\text{O}_3\text{N}$ requires $\text{M.W.}=235$.

The silver salt, prepared in the usual manner, is a yellow, amorphous precipitate, which darkens rapidly on exposure to air and light:

0.2618 gave 0.0828 Ag. $\text{Ag}=31.62$.

$\text{C}_{13}\text{H}_{16}\text{O}_3\text{NAg}$ requires $\text{Ag}=31.58$ per cent.

Ethyl 3-anilino-1:1-dimethyl- Δ^3 -cyclohexenyldene-5-acetate, prepared by heating ethyl hydroxydimethylcyclohexenyldenecyano-

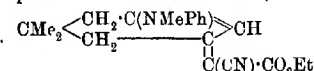


acetate with aniline, is readily soluble in acetone, alcohol, or acetic acid, insoluble or only slightly soluble in light petroleum, benzene, or chloroform, and crystallises from methyl alcohol in felted masses of long, feathery, golden-yellow needles, melting at 197° :

0.2006 gave 14.6 c.c. N_2 (moist) at 6° and 752 mm. $\text{N}=8.77$.

$\text{C}_{19}\text{H}_{22}\text{O}_2\text{N}_2$ requires $\text{N}=9.03$ per cent.

Ethyl 3-methylanilino-1:1-dimethyl- Δ^3 -cyclohexenyldene-5-cyanoacetate was prepared in a similar manner, using methylaniline



instead of aniline. It separates from methyl alcohol in small, transparent, flattened, yellow crystals, melting at 183° :

0.2135 gave 15.2 c.c. N_2 (moist) at 8° and 754 mm. $N = 8.64$.

$$\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2 \text{ requires N} = 8.64 \text{ per cent.}$$

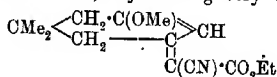
Hydrolysis of Ethyl Hydroxydimethylcyclohexenylidenecyanoacetate.

Ten grams of the ester were boiled with 100 c.c. of concentrated hydrochloric acid for six hours, when the solid slowly dissolved and an oil separated. The liquid was then diluted with water, extracted with ether, the ethereal solution washed, dried, and evaporated, and the residue distilled under a pressure of 23 mm., when nearly the whole (5.5 grams) distilled at 100—103°. It possessed the characteristic odour of trimethylcyclohexenone (b. p. 109°/32 mm., compare Trans., 1909, 95, 24), and its identity with this substance was established by preparing from it the oxime, which melted at 78°, and the semicarbazone, which melted at 193° ($N=21.55$; $C_{10}H_{17}ON_3$ requires $N=21.54$ per cent.). The melting points of the above derivatives remained unaltered on mixing with an equal quantity of the corresponding substances prepared in the manner previously described (*loc. cit.*).

Esterification of Ethyl Hydroxydimethylcyclohexenylidenecyanoacetate.—1. *With Methyl Alcohol and Sulphuric Acid.*

Ten grams of the hydroxy-compound were heated on the water-bath with 100 c.c. of a 5 per cent. solution of sulphuric acid in absolute alcohol for three hours. The whole was then poured into water, extracted four times with ether, the ethereal solution washed with a dilute solution of sodium hydroxide to remove traces of esterified material, then with water, dried, and evaporated. The solid residue (10 grams) was separated by fractional crystallisation from light petroleum (b. p. 60—80°) into two isomeric substances A and B, melting respectively at 79° and 90°. No very exact figures can be given as to the relative proportions in which these two esters are formed, but A predominates, probably to the extent of five to six times the amount of B.

Ethyl 3-methoxy-1:1-dimethyl-Δ³-cyclohexenylidene-5-cyanoacetate (A) separates out first, crystallising very readily in small,



white, elongated needles, melting at 79°:

0.1255 gave 0.3112 CO_2 and 0.0869 H_2O . $\text{C}=67.62$; $\text{H}=7.69$.

$C_{14}H_{19}O_3N$ requires C=67.47; H=7.63 per cent.

The isomeric ester **B** is contained in the mother liquors of **A**, and,

after repeated fractional crystallisation, separates in thin, white flakes, melting at 90° .

0.1486 gave 0.2696 CO_2 and 0.1022 H_2O . $\text{C}=67.83$; $\text{H}=7.64$.
 $\text{C}_{16}\text{H}_{20}\text{O}_3\text{N}$ requires $\text{C}=67.47$; $\text{H}=7.63$ per cent.

2. With Ethyl Alcohol and Sulphuric Acid.

Ten grams of the hydroxy-compound were esterified exactly as described above, using ethyl instead of methyl alcohol, when 12.6 grams of a mixture of two esters were obtained, which were separated by fractional crystallisation from methyl alcohol into two substances, A and B, melting respectively at 106° and 97° . The relative proportions produced are much the same as in the case of the methyl esters, the isomeric form A predominating in amount.

Ethyl ethoxy-1:1-dimethyl- Δ^4 -cyclohexenylidene-5-cyanoacetate (A) crystallises from methyl alcohol in small, white needles, or from light petroleum (b. p. $60-80^\circ$) in clusters of beautiful elongated, prismatic needles, melting at 106° :

0.1280 gave 0.3215 CO_2 and 0.0958 H_2O . $\text{C}=68.50$; $\text{H}=8.31$.

0.3218 „ 15.2 c.c. N_2 (moist) at 10° and 744 mm. $\text{N}=5.53$.

$\text{C}_{15}\text{H}_{21}\text{O}_3\text{N}$ requires $\text{C}=68.44$; $\text{H}=7.98$; $\text{N}=5.32$ per cent.

The molecular weight was determined by the cryoscopic method, using benzene as solvent:

Found, M.W.=235. $\text{C}_{15}\text{H}_{21}\text{O}_3\text{N}$ requires M.W.=263.

This ester has also been prepared by the action of ethyl iodide on the sodium salt of ethyl hydroxydimethylcyclohexenylidenecyanoacetate in alcoholic and in benzene solution; but the amount of pure material produced was very small, resinous products being formed, and under the conditions employed it was not found possible to isolate any of the isomeric ester melting at 97° .

The isomeric ester B, obtained from the mother liquors of A, crystallises from methyl alcohol in lustrous, transparent prisms, melting at 97° :

0.1035 gave 0.2606 CO_2 and 0.0758 H_2O . $\text{C}=68.66$; $\text{H}=8.14$.

$\text{C}_{16}\text{H}_{21}\text{O}_3\text{N}$ requires $\text{C}=68.44$; $\text{H}=7.98$ per cent.

The molecular weight, determined by the same method as used in the case of the isomeric ester, was found to be 236.

Although the observed values for the molecular weights of the two esters do not show as close an agreement with the theoretical value as might be desired, they are nevertheless of the same order, and serve to prove that the isomerism of these two substances is not due to the formation of complex molecules, but is in all probability a case of *cis-trans*-isomerism.

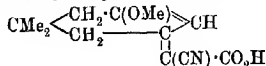
Hydrolysis of Ethyl Methoxydimethylcyclohexenylidenecyanoacetate.

Experiment showed that the same substance (m. p. 174°) was the sole product obtained when either of the esters, melting respectively at 79° and 90° , was hydrolysed with methyl-alcoholic potassium hydroxide, and therefore, for the purpose of investigating the nature of the substance melting at 174° , there was no object in first separating the two esters by the tedious process of fractional crystallisation. Four grams of the mixture of the two isomeric esters were therefore heated for two hours on the water-bath with 3 grams of potassium hydroxide dissolved in 60 c.c. of absolute methyl alcohol, when the solution was diluted with water and extracted once with ether, to remove any traces of unaltered ester. The aqueous solution was next acidified with sulphuric acid extracted three times with ether, and the ethereal solution washed dried, and evaporated. There resulted 3 grams of a solid, which was purified by crystallisation from dilute methyl alcohol, and analysed:

0.1380 gave 0.3318 CO_2 and 0.0841 H_2O . $\text{C} = 65.57$; $\text{H} = 6.77$.

$\text{C}_{12}\text{H}_{15}\text{O}_3\text{N}$ requires $\text{C} = 65.16$; $\text{H} = 6.78$ per cent.

3-Methoxy-1: 1-dimethyl- Δ^3 -cyclohexenylidene-5-cyanoacetic acid



crystallises from dilute methyl alcohol in masses of irregular plates, melting at 174° . At 179° a steady evolution of carbon dioxide occurs, with production of methoxydimethylcyclohexenylidenecyanoacetonitrile (compare the hydrolysis of the corresponding ethoxy derivative, p. 531).

The presence of a methoxyl group in this acid was confirmed by a Zeisel determination:

0.2353 gave 0.2424 AgI . $\text{OMe} = 13.6$.

$\text{C}_{12}\text{H}_{15}\text{O}_3\text{N}$ requires $\text{OMe} = 14.00$ per cent.

It is interesting to note that when the hydrolysis of ethyl methoxydimethylcyclohexenylidenecyanoacetate is carried out in ethyl-alcoholic solution, the methyl of the methoxyl group is replaced by an ethyl group, the product being ethoxydimethylcyclohexenylidenecyanoacetic acid, melting at 149° (compare p. 531).

Hydrolysis of Ethyl Ethoxydimethylcyclohexenylidenecyanoacetate.

The following experiments were carried out both with the ester A, melting at 106° , and with the ester B, melting at 97° , and as

the products of hydrolysis are the same, no matter which of the two isomerides is employed, the description of the experiments applies to either of them.

1. *With Hydrochloric Acid.*—Eight and a-half grams of the ester were heated with 100 c.c. of concentrated hydrochloric acid under a reversed condenser for five hours, when, after extracting with ether and working up in the usual way, 5 grams of an oil were obtained, boiling at 104—107°/25 mm. This fraction was identified as trimethylcyclohexenone by preparing from it the semicarbazone, which melted at 193°, and the oxime, which melted at 77—78°.

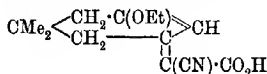
2. *With Potassium Hydroxide.*—Twenty-four grams of the ester were heated for two hours on the water-bath with 15 grams of potassium hydroxide dissolved in 200 c.c. of ethyl alcohol (if methyl alcohol is employed instead of ethyl alcohol, methoxydimethylcyclohexenylidenecyanoacetic acid is the product), and the product worked up as described in the case of ethyl methoxydimethylcyclohexenylidenecyanoacetate (see page 530), when a solid was obtained, which was crystallised from aqueous alcohol and analysed:

0.1114 gave 0.2718 CO₂ and 0.0731 H₂O. C=66.54; H=7.29.

0.2009 „ 9.4 c.c. N₂ (moist) at 8° and 752 mm. N=5.59.

C₁₈H₁₇O₃N requires C=66.38; H=7.23; N=5.95 per cent.

3-Ethoxy-1:1-dimethyl- Δ^3 -cyclohexenylidene-5-cyanoacetic acid is readily soluble in all the ordinary organic solvents, except light



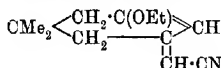
petroleum. It crystallises from aqueous methyl or ethyl alcohol in clusters of minute needles, which melt and decompose at 149°, gas being steadily evolved at 153°.

The molecular weight was determined by titration against standard potassium hydroxide solution, using phenolphthalein as indicator:

0.1901 required 7.92 c.c. N/10-KOH. Calculated, 8.09 c.c.

Found, M.W.=240. C₁₈H₁₇O₃N requires M.W.=235.

3-Ethoxy-1:1-dimethyl- Δ^3 -cyclohexenylidene-5-acetonitrile was prepared by heating 5 grams of ethoxydimethylcyclohexenylidene-



cyanoacetic acid under diminished pressure. A little above the melting point of the acid, carbon dioxide was given off, and as

soon as the evolution had ceased, the residual liquid was distilled, when the whole (3.7 grams) boiled at 162–164°/18 mm.:

0.2272 gave 13.2 c.c. N_2 (moist) at 8° and 768 mm. $N=7.10$.

$C_{12}H_{17}ON$ requires $N=7.32$ per cent.

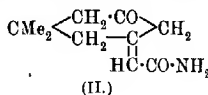
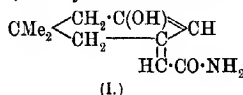
The pure substance is a colourless, highly refractive, oily liquid, boiling at 163°/18 mm., and possessing an odour of hydrocyanic acid. A Zeisel determination, carried out according to Perkin's modified method, gave the following result:

0.2468 gave 0.2745 AgI. $OEt=21.3$.

$C_{12}H_{17}ON$ requires $OEt=23.5$ per cent.

This result is somewhat low, but various investigators have found that ethoxyl determinations generally come out from 1 to 2 per cent. below the calculated figure.

The nitrile is only very slowly attacked by potassium hydroxide in alcoholic solution, giving a small amount of a substance crystallising from a mixture of chloroform and light petroleum, melting at 130°, and giving, on analysis, numbers agreeing with a formula $C_{10}H_{15}O_2N$. It is probably, hydroxydimethylcyclohexenylideneacetamide (I), or, as it is devoid of any acid nature, it may be this substance in the isomeric ketonic form (II).



When heated with concentrated hydrochloric acid, 8.5 grams of the nitrile gave 5 grams of a liquid having a camphoraceous odour, and boiling constantly at 105°/25 mm. This substance was identified as trimethylcyclohexenone by preparing the oxime, which melted at 78°, nor was this melting point lowered by admixture with an equal quantity of the oxime of pure trimethylcyclohexenone.

Action of Ethyl Methylcyanoacetate on Chlorodimethylcyclohexenone.

Ethyl methylcyanoacetate was prepared by the interaction of ethyl sodiocyanoacetate and methyl iodide, according to the directions of Auwers (*Annalen*, 1895, **285**, 283). The product, although stated by Auwers to be pure ($N=10.93$; calculated, 11.02 per cent.), boiled for the most part at 190–195°, and subsequent experiments showed that it undoubtedly contained considerable amounts of ethyl cyanoacetate and also ethyl dimethylcyanoacetate, which substances, if present in equivalent amounts, would account for the correct value for nitrogen quoted by Auwers.

Twenty-four grams of chlorodimethylcyclohexenone were added to a mixture of 39 grams (2 mols.) of ethyl methylcyanoacetate and 7 grams of sodium (2 atoms) dissolved in 42 c.c. of absolute ethyl alcohol. After heating on a water-bath for six hours, the reaction mixture was poured into water, extracted four times with ether (aqueous solution = A), the ethereal solution washed, dried, evaporated, and the residual liquid distilled in a current of steam, when all but a negligible quantity of a sticky resin passed over.

The distillate, after extraction with ether, etc., yielded 24 grams of a liquid, which, after repeated fractionation, gave two main portions of about equal weight, boiling at 126—127° and 190—195°, the latter consisting of ethyl methylcyanoacetate.

The fraction 126—127°, from its odour and boiling point, appeared to be ethyl carbonate, and its identity with that substance was established by analysis:

0.1406 gave 0.2629 CO_2 and 0.1068 H_2O . $\text{C} = 50.99$; $\text{H} = 8.44$.

$\text{C}_5\text{H}_{10}\text{O}_3$ requires $\text{C} = 50.85$; $\text{H} = 8.47$ per cent.

The above-mentioned aqueous alkaline solution A was acidified with sulphuric acid, extracted with ether, and, after working up in the usual manner, yielded 32 grams of a viscid, oily liquid, which, after some time, partly solidified. The solid (5 grams) was separated by spreading on porous plate, and, after crystallisation from benzene, melted at 141°, nor was this melting point altered on mixing with ethyl hydroxydimethylcyclohexenylidenecyanoacetate (see p. 528). The formation of this ester is undoubtedly due to the unchanged ethyl cyanoacetate contained in the ethyl methylcyanoacetate employed.

The oil, recovered from the porous plate by extraction with ether, did not further solidify, and could not be distilled, even under diminished pressure, without decomposing. It was therefore esterified by boiling for four hours with 300 c.c. of ethyl alcohol containing 5 per cent. of sulphuric acid. The resulting solution was worked up as already described, and the residue (18 grams) distilled under 32 mm. pressure, when the following fractions were collected:

100—150° = 3.7 grams;	150—170° = 0.4 gram;
170—195° = 6.5 grams;	195—220° = 2.4 grams.

The fraction 100—150° consisted principally of ethyl dimethylmalonate, for on hydrolysis it yielded dimethylmalonic acid, melting at 193° with evolution of gas:

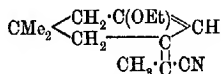
0.1088 gave 0.1824 CO_2 and 0.0597 H_2O . $\text{C} = 45.72$; $\text{H} = 6.10$.

$\text{C}_6\text{H}_8\text{O}_4$ requires $\text{C} = 45.45$; $\text{H} = 6.06$ per cent.

The presence of ethyl dimethylmalonate proves that the original

ethyl methylcyanoacetate must have contained some ethyl dimethylcyanoacetate.

The fraction 170—195°, on redistillation, passed over as a pale yellow, refractive, oily liquid, and although it did not boil very constantly (170—180°/27 mm.), analysis and subsequent hydrolysis proved it to consist of 3-ethoxy-1:1-dimethyl- Δ^8 -cyclohexenylidene-5-propionitrile:

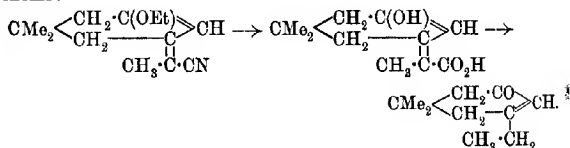


0.1145 gave 0.3178 CO_2 and 0.0951 H_2O . $\text{C} = 75.70$; $\text{H} = 9.23$.

$\text{C}_{10}\text{H}_{16}\text{ON}$ requires $\text{C} = 76.09$; $\text{H} = 9.26$ per cent.

The mechanism of the reaction giving rise to the corresponding hydroxydimethylcyclohexenylidenepropionitrile has been already explained (see p. 524).

Seven grams of the above nitrile were heated with 100 c.c. of concentrated hydrochloric acid for five hours under a reversed condenser. The product was poured into water, extracted four times with ether, the ethereal solution washed first with sodium hydroxide solution, then with water, dried, evaporated, and the residue (5 grams) distilled, when it boiled constantly at 119.5°/25 mm. as a colourless, refractive liquid, which proved to be dimethylethylcyclohexenone (compare *Trans.*, 1909, **95**, 28), the formation of which substance takes place in accordance with the following scheme:



0.1371 gave 0.3952 CO_2 and 0.1312 H_2O . $\text{C} = 78.61$; $\text{H} = 10.63$.

$\text{C}_{10}\text{H}_{16}\text{O}$ requires $\text{C} = 78.94$; $\text{H} = 10.53$ per cent.

The oxime, prepared in the usual manner, is a viscid, oily liquid, boiling at 153°/28 mm., and solidifying on cooling to radiating clusters of flattened, transparent needles, melting at 43—45°. It is so readily soluble in all the ordinary organic solvents that it was found to be most easily purified by distillation:

0.1921 gave 14 c.c. N_2 (moist) at 18° and 763 mm. $\text{N} = 8.45$.

$\text{C}_{10}\text{H}_{17}\text{ON}$ requires $\text{N} = 8.38$ per cent.

As this oxime has not been previously described, a specimen was made for the purpose of comparison from pure dimethylethylcyclohexenone, obtained in the manner formerly described (*loc. cit.*).

It was found to possess properties identical with the above-mentioned oxime.

The fraction 195—230° solidified after some time. After one crystallisation from benzene, it melted at 106°, and proved to be ethyl ethoxydimethylcyclohexenylidenecyanoacetate (see page 529). It was mentioned on page 533 that when the aqueous alkaline liquid A was acidified with sulphuric acid, 5 grams of ethyl hydroxydimethylcyclohexenylidenecyanoacetate separated, but evidently this separation is not a complete one, and the unaltered material is converted into its ethyl ether (m. p. 106°) during the process of esterification to which the residue was submitted.

Action of Ethyl Acetoacetate on Chlorodimethylcyclohexenone.

Fifty-two grams (2 mols.) of freshly distilled ethyl acetoacetate were mixed with a solution of 9.2 grams of sodium (2 atoms) in 110 c.c. of absolute alcohol, and 32 grams (1 mol.) of chlorodimethylcyclohexenone added. The resulting red liquid was transferred to two soda-water bottles, which were securely corked, and then heated in a boiling-water bath for two hours. The reaction mixture was poured into water, extracted five times with ether, and the ethereal solution washed, dried, and fractionated, using a Young's rod-and-disk still-head. When the ether had passed over, a small quantity of a liquid boiling at 65—70° (residue=A) was obtained, which, after further purification, was proved to consist of ethyl acetate.

The residue A was distilled in a current of steam to remove unaltered ethyl acetoacetate, and the non-volatile portion extracted three times with ether, the ethereal solution dried and evaporated, and the residue distilled, when nearly the whole (18 grams) passed over at 181°/27 mm.:

0.1242 gave 0.3106 CO_2 and 0.0972 H_2O . $\text{C}=68.20$; $\text{H}=8.69$.

$\text{C}_{12}\text{H}_{18}\text{O}_3$ requires $\text{C}=68.57$; $\text{H}=8.57$ per cent.

These numbers indicated that the substance was ethyl 1:1-dimethyl- Δ^4 -cyclohexen-3-one-5-acetate (Trans., 1909, 95, 23), and the identity of the two liquids was established by hydrolysing the above product with alcoholic potassium hydroxide (*loc. cit.*), when it yielded trimethylcyclohexen-3-one, boiling at 99°/18 mm., characterised by the preparation of its oxime, which melted at 77—78°.

The authors take this opportunity of expressing their thanks to the Research Fund Committee of the Chemical Society for a grant which has, in part, defrayed the expenses of this investigation.

RESEARCH LABORATORY, PHARMACEUTICAL SOCIETY,
17, BLOOMSBURY SQUARE, W.C.

LVII.—*The Influence of Colloids and Fine Suspensions on the Solubility of Gases in Water. Part I. Solubility of Carbon Dioxide and Nitrous Oxide.*

By ALEXANDER FINDLAY and HENRY JERMAIN MAUDE CREIGHTON,
M.A., M.Sc. (1851 Exhibition Science Scholar of Dalhousie
University, Halifax, Nova Scotia).

For many years the problem of the absorption of gases, more especially of oxygen and carbon dioxide, by blood has claimed the attention of physiologists. In the case of oxygen the absorption has been regarded as being due, in greatest measure, to the formation of a compound with the hæmoglobin of the blood; whereas, in the case of carbon dioxide, the increased absorption as compared with a corresponding salt solution has been attributed to the reputed alkalinity of the blood, and the consequent formation of carbonate and bicarbonate.

In recent years, however, different investigators (compare Hoerber, *Pflüger's Archiv*, 1903, **99**, 572; Farkas, *ibid.*, 1903, **98**, 551; Friedenthal, *Verworn's Archiv f. allgem. Physiologie*, 1904, **4**, 44; van Westenryk, *Arch. exp. Path. Pharm. Suppl.*, 1908, p. 517) have shown by different methods that blood-serum is practically "water-neutral." In view of these results, it seemed that possibly the absorption of carbon dioxide by the blood had been ascribed too exclusively to the alkalinity of blood, and it seemed not improbable that the colloids present in blood play an important rôle (Findlay and Harby, *Zeitsch. Chem. Ind. Kolloide*, 1908, **3**, 169; Wo. Ostwald, *ibid.*, 1908, **2**, 264). Before this view could be tested, it was necessary to study the influence of colloids of various kinds on the absorption of gases, since our knowledge of this depended almost entirely on the few experiments carried out by Geffcken (*Zeitsch. physikal. Chem.*, 1904, **49**, 298).

Preliminary experiments had shown that the increased absorption of carbon dioxide which occurred under atmospheric pressure in presence of certain colloids was due, probably, to chemical interaction. To obtain a deeper insight into the influence of colloids on gas solubility, it was deemed of importance to study the solubility under a series of pressures, and also to exclude effects due to chemical combination by studying the absorption of a neutral gas, nitrous oxide (with regard to the neutrality of nitrous oxide, see Geffcken, *loc. cit.*, p. 301). This gas was chosen because its solubility in water is nearly the same as that of carbon dioxide. Experiments on the lines indicated were carried out during the year 1908-9, the influence of ferric hydroxide, gelatin, arsenious sulphide, silicic acid,

dextrin, starch, glycogen, egg-albumen, and serum-albumen, as well as suspensions of charcoal and silica, on the absorption of carbon dioxide and nitrous oxide having been investigated at pressures varying from about 750 mm. to 1400 mm. of mercury.

Apparatus.

The apparatus employed was, in its essential points, the same as that used by Geffcken (*loc. cit.*), the manometer tube, however, being graduated and considerably lengthened to permit of absorptions being carried out at pressures higher than atmospheric. The burette was connected with the absorption pipette by means of capillary copper tubing, in order to impart the necessary flexibility to the apparatus. The burette was contained in a glass mantle through which water was caused to circulate, the temperature being maintained constant within 0.1° throughout a determination.

So long as the absorption of gas was allowed to take place under atmospheric pressure only, the dead space (that is, the ungraduated portion at the top of the burette and the volume of the tubes connecting it with the absorption vessel) does not require to be taken account of, as the initial and final conditions under which the gas is measured are the same. When, however, the absorption is allowed to take place at higher pressures, the volume of the dead space must be known. This was ascertained by measuring the total contraction of a known volume of gas and the volume in the dead space, produced by a known increase of pressure.

Since the gas in the measuring burette was always kept dry, the point of saturation of the solution with gas was approached from the side of least pressure only, but precautions were taken to make sure that the process of absorption at any given pressure was complete.

The liquid used for the absorption of the gas was previously well boiled to free it from air; or in those cases where boiling was not permissible, the liquid was freed from air by being placed under diminished pressure.

In all the following experiments the temperature of absorption was 25.0° , and the experimental error did not exceed ± 0.25 per cent., and was in most cases less than this.

Calculation of Results.

The solubility was calculated by means of the formula:

$$\text{Solubility} = \frac{C_1}{C_2} = \frac{\left[\left(\frac{v_1 P}{P+p} \cdot \frac{T}{T_1} - \frac{v_2 T}{T_2} \right) \left(\frac{P+p}{P+p-p'} \right) \right]}{V_2} - V_1,$$

where

C_l = concentration of the gas in the liquid phase.

C_g = " " " " " gaseous phase.

v_1 = initial volume of the gas in the burette measured at the pressure P .

v_2 = final volume of the gas in the burette measured under the pressure $P + p$.

T = absolute temperature of experiment (thermostat temperature).

T_1 = absolute temperature of the gas in the burette at the beginning of the experiment when v_1 was measured.

T_2 = absolute temperature of the gas in the burette at the end of the experiment when v_2 was measured.

P = barometric pressure.

p = increase of pressure as shown by the manometer.

p' = vapour pressure of the liquid in the absorption pipette at the temperature T .

V_1 = volume of the gas space in the pipette at the temperature T .

V_2 = volume of absorbing liquid in the pipette.

The volume v_2 was corrected, when necessary, for the dead space of the apparatus. Considering the experimental errors of determination, no correction was applied to the burette readings for cubical expansion of glass, nor were the barometric readings corrected for temperature.

I.—Solubility of Carbon Dioxide.

The carbon dioxide employed for the following experiments was the commercial product, which analysis showed to contain 0.58 per cent. of impurity. The following values were found for its solubility in pure water at 25° (table I):

TABLE 1.—Solubility of Carbon Dioxide in Water.

Pressure (mm. Hg) ...	752	800	955	1059	1153	1351
Solubility	0.817	0.815	0.816	0.817	0.818	0.820
Pressure	743	841	955	1064	1243	1351
Solubility	0.816	0.817	0.817	0.819	0.819	0.820

As the mean of these and a number of other determinations we obtained the value 0.817 for the solubility of the carbon dioxide employed, the solubility being independent of the pressure within the limits of experimental error. The value found by Geffcken for pure carbon dioxide was 0.826.

b) Ferric Hydroxide Solution.

In preparing the solution of ferric hydroxide, the method recommended by A. A. Noyes (*J. Amer. Chem. Soc.*, 1905, 37, 94) was employed. To a molar solution of ferric chloride, molar ammonium carbonate solution was added until the precipitate which formed on each addition barely dissolved. This mixture was then thoroughly dialysed, first against tap water, and finally against distilled water, until soluble salts were removed. The concentration of the solution was determined by precipitation of the hydroxide with ammonium sulphate.

FIG. 1.

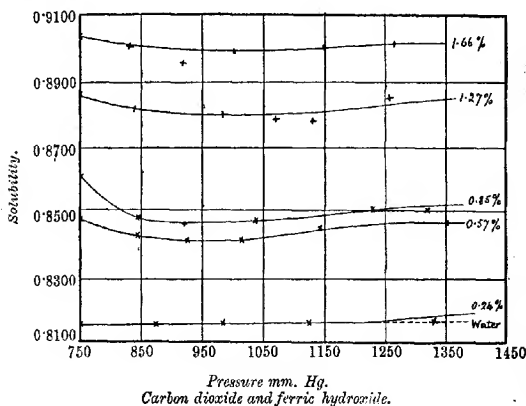


TABLE 2.—Solubility of Carbon Dioxide in Ferric Hydroxide Solutions (see Fig. 1).

Concentration: 0.569 gram of $\text{Fe}(\text{OH})_3$ in 100 c.c. of solution.
Density = 1.000.

Pressure	750	846	928	1015	1146	1356
Solubility	0.848	0.843	0.841	0.841	0.845	0.846

Concentration: 0.854 gram of $\text{Fe}(\text{OH})_3$ in 100 c.c. of solution.
Density = 1.003.

Pressure	750	847	928	1040	1234	1322
Solubility	0.862	0.858	0.856	0.857	0.860	0.861

Concentration: 1.277 gram of $\text{Fe}(\text{OH})_3$ in 100 c.c. of solution.
Density = 1.005.

Pressure	746	841	985	1071	1133	1256
Solubility	0.886	0.881	0.880	0.878	0.878	0.887

TABLE 2 (continued).

Concentration: 1.661 grams of $\text{Fe}(\text{OH})_3$ in 100 c.c. of solution.
Density = 1.009.

Pressure	747	831	918	1002	1150	1267
Solubility	0.804	0.901	0.896	0.900	0.900	0.902

Geffcken (*loc. cit.*) has stated that the comparatively rapid initial absorption of carbon dioxide is succeeded by a slow further absorption. In our experiments this slow absorption was barely appreciable except at higher pressures, and was, even then, not great.

The above numbers, when plotted, show that the increase of solubility under atmospheric pressure is proportional to the concentration of the ferric hydroxide.

(b) Dextrin.

The dextrin employed was the purest supplied by Kahlbaum. It contained a slight quantity of impurity insoluble in water, and this was separated from the solutions before they were used for absorbing carbon dioxide. The solubility values are given in table 3.

TABLE 3.—Solubility of Carbon Dioxide in Dextrin Solutions.
(See also Fig. 2).

Concentration: 3.50 grams of dextrin in 100 c.c. of solution.
Density = 1.008.

Pressure	753	819	888	1060	1171	1262
Solubility	0.799	0.800	0.800	0.800	0.801	0.803

Concentration: 5.60 grams in 100 c.c. of solution. Density = 1.015.

Pressure	754	806	856	971	1078	1247
Solubility	0.785	0.785	0.784	0.787	0.787	0.791

Concentration: 9.50 grams in 100 c.c. of solution. Density = 1.034.

Pressure	753	817	864	960	1115	1286
Solubility	0.761	0.756	0.753	0.759	0.764	0.768

Concentration: 13.00 grams in 100 c.c. of solution. Density = 1.040.

Pressure	741	798	882	962	1181	1256
Solubility	0.746	0.741	0.742	0.745	0.749	0.751

Concentration: 18.90 grams in 100 c.c. of solution. Density = 1.064.

Pressure	748	846	934	1031	1180	1344
Solubility	0.715	0.710	0.713	0.716	0.720	0.725

Concentration: 20.60 grams in 100 c.c. of solution. Density = 1.069.

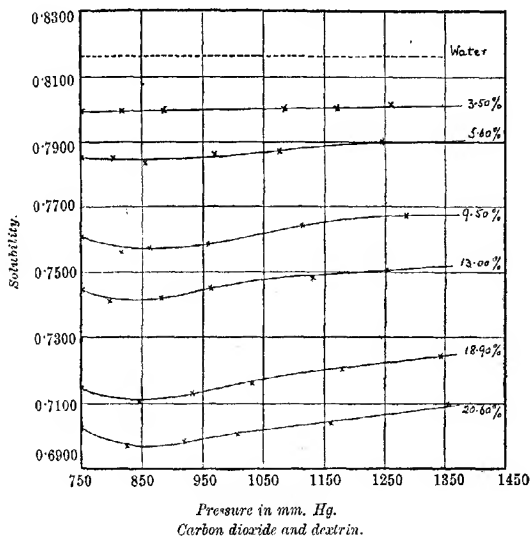
Pressure	728	826	920	1008	1161	1356
Solubility	0.703	0.697	0.698	0.700	0.704	0.710

As shown in Fig. 8, the solubility diminishes in almost exact proportionality with the increase in concentration of the dextrin.

(c) Arsenious Sulphide.

The arsenious sulphide was prepared by passing hydrogen sulphide into a solution of pure arsenious oxide until the latter was saturated. The greater part of the excess of hydrogen sulphide was then expelled by bubbling hydrogen through the liquid, which was then filtered before being used. As colloidal solutions of arsenious

FIG. 2.



sulphide decompose on boiling, the last traces of dissolved air were removed by placing the liquid under diminished pressure, although this led to the formation of a very thin film on the surface of the liquid. This behaviour is similar to the formation of films on the surface of peptone solutions observed by Metcalf (*Zeitsch. physikal. Chem.*, 1905, 52, 1), and is no doubt to be regarded similarly as an illustration of Gibbs's principle of increased surface concentration.

The amount of arsenious sulphide in the solutions was determined

precipitating with hydrochloric acid and drying the precipitate 80°.

TABLE 4.—*Solubility of Carbon Dioxide in Solutions of Arsenious Sulphide.*

Concentration: 0.392 gram of As_2S_3 in 100 c.c. of solution.
Density = 0.997.

Pressure	756	891	951	1047	1172	1259
Solubility	0.816	0.817	0.814	0.816	0.818	0.820

Concentration: 1.410 grams in 100 c.c. of solution. Density = 1.003.

Pressure	756	851	972	1082	1187	1281
Solubility	0.810	0.810	0.812	0.810	0.812	0.811

Concentration: 2.289 grams in 100 c.c. of solution. Density = 1.007.

Pressure	754	853	953	1003	1068	1211
Solubility	0.806	0.806	0.806	0.806	0.806	0.806

(d) *Starch.*

For these experiments Kahlbaum's pure soluble starch was employed.

TABLE 5.—*Solubility of Carbon Dioxide in Solutions of Starch.*
(See also Fig. 3.)

Concentration: 2.50 grams of starch in 100 c.c. of solution.
Density = 1.009.

Pressure	752	849	951	1050	1182	1334
Solubility	0.796	0.797	0.799	0.801	0.804	0.806

Concentration: 5.00 grams in 100 c.c. of solution. Density = 1.016.

Pressure	753	840	912	1021	1193	1298
Solubility	0.778	0.780	0.781	0.784	0.789	0.790

Concentration: 7.50 grams in 100 c.c. of solution. Density = 1.023.

Pressure	752	860	1016	1078	1201	1351
Solubility	0.762	0.764	0.767	0.769	0.772	0.774

Concentration: 10.00 grams in 100 c.c. of solution. Density = 1.030.

Pressure	753	893	982	1087	1163	1337
Solubility	0.750	0.753	0.754	0.756	0.759	0.760

It was observed in the case of the above solutions that the time required to saturate the solution with gas was much greater than in most of the other cases studied. The relation between starch concentration and solubility is shown in Fig. 8.

(e) Gelatin.

French sheet gelatin, which was found to be free from salts, was used. Solutions containing as much as 6 per cent. of gelatin were quite mobile at 25°.

Fig. 3.

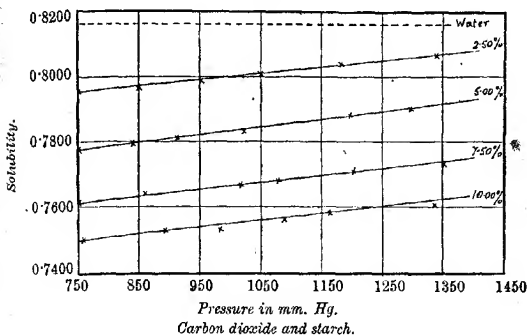


TABLE 6.—*Solubility of Carbon Dioxide in Solutions of Gelatin.*
See also Fig. 4.)

Concentration: 1.06 grams of gelatin in 100 c.c. of solution.
Density = 0.999.

Pressure	746	825	901	1011	1184	1369
Solubility	0.815	0.814	0.814	0.815	0.815	0.815

Concentration: 1.68 grams in 100 c.c. of solution. Density = 1.000.

Pressure	740	837	938	1072	1219	1324
Solubility	0.819	0.816	0.816	0.816	0.817	0.817

Concentration: 3.36 grams in 100 c.c. of solution. Density = 1.003.

Pressure	741	826	943	1068	1220	1387
Solubility	0.826	0.819	0.818	0.818	0.819	0.820

Concentration: 6.09 grams in 100 c.c. of solution. Density = 1.008.

Pressure	746	836	936	1045	1194	1371
Solubility	0.835	0.827	0.824	0.824	0.825	0.826

The influence of concentration of gelatin on the solubility at atmospheric pressure is shown in Fig. 7.

Although dilute solutions of gelatin quickly become saturated with gas, the absorption takes place more slowly in the case of the more concentrated solutions. On reducing the pressure, the gas escaped rapidly from the solution, so as to cause considerable frothing. The question of rate of evolution of gas is, however, a

special one, and, on account of its importance in various directions, will require to be investigated specially.

Further, absorption of carbon dioxide appreciably lowered the gelatinising temperature of the solution, thus producing an effect similar to peptonisation. Whether the effect is a temporary or a permanent one, we have not yet investigated.

(f) *Glycogen.*

Kahlbaum's pure glycogen was employed. In order to free it from the small quantities of the salts which it contained, it was subjected to dialysis, toluene being added to prevent putrefaction.

FIG. 4.

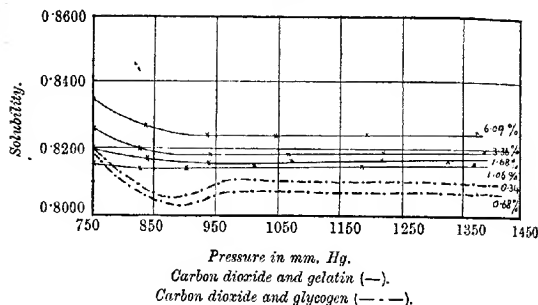


TABLE 7.—*Solubility of Carbon Dioxide in Solutions of Glycogen*
(see also Fig. 4).

Concentration: 0.34 gram of glycogen in 100 c.c. of solution.
Density=0.998.

Pressure	759	859	959	1132	1247	1369
Solubility ..	0.819	0.805	0.810	0.812	0.810	0.810

Concentration: 0.68 gram in 100 c.c. of solution. Density=1.000.

Pressure	759	842	954	1114	1277	1371
Solubility ..	0.817	0.805	0.807	0.807	0.807	0.807

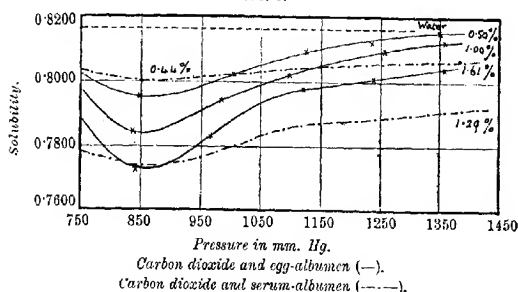
As it was impossible to remove all the toluene from the glycogen solutions, the experimental values of the solubility had to be corrected for the slight lowering of solubility produced by the toluene. The numbers in the above table are such corrected values, but they are probably not quite so accurate as in the previous cases. We may assume, however, that the relative values at different pressures and concentrations are unaffected by the correction.

(g) *Egg-Albumen.*

This was prepared from fresh eggs by the improved method of Holmeister (*J. Physiol.*, 1898, **23**, 130). Pure crystals were obtained from the first crystalline precipitate as follows. The precipitate was washed with three changes of half saturated ammonium sulphate solution, which contained one part of glacial acetic acid per thousand. The crystals were then dissolved in the minimal quantity of water, and, while constantly stirring, a saturated solution of ammonium sulphate was added slowly until a distinct precipitate was formed; then, in addition, further 2 c.c. of the sulphate solution were added for each 1000 c.c. of albumen solution. At the end of several days crystals were obtained.

As these crystals are not pure albumen, but contain ammonium sulphate either in combination or in solution, they were dissolved

Fig. 5.



in water and dialysed until free from ammonium salts. A small quantity of toluene was added to prevent putrefaction.

The amount of albumen in solution was determined by heating the solution until the albumen was completely coagulated, the coagulum being then dried at 100° and weighed.

TABLE 8.—*Solubility of Carbon Dioxide in Solutions of Egg-Albumen* (see also Fig. 5).

Concentration: 0.50 gram of albumen in 100 c.c. of solution.
Density = 0.999.

Pressure	729	849	1004	1125	1236	1350
Solubility	0.806	0.795	0.802	0.810	0.812	0.816

Concentration: 1.00 gram in 100 c.c. of solution. Density = 1.002.

Pressure	734	836	984	1089	1257	1358
Solubility	0.800	0.784	0.794	0.801	0.810	0.812

TABLE 8 (continued)

Concentration: 1.61 grams in 100 c.c. of solution. Density = 1.005.

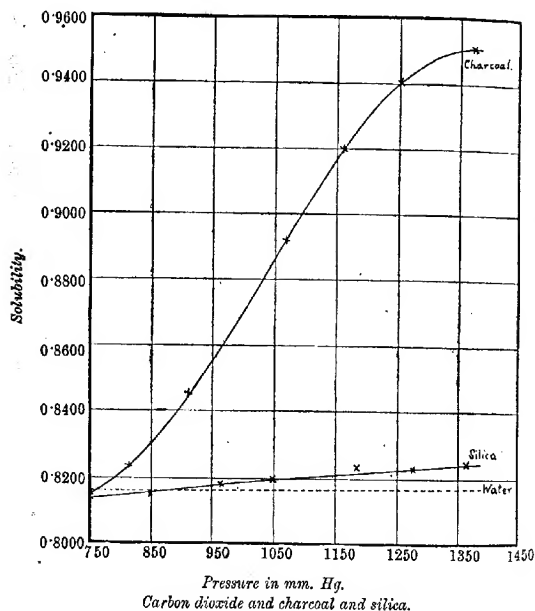
Pressure	738	841	908	1123	1239	1359
Solubility	0.791	0.773	0.783	0.797	0.801	0.804

The influence of concentration of albumen on the solubility at atmospheric pressure is shown in Fig. 7.

(h) Serum-Albumen.

Neutral serum-albumen was prepared from fresh ox-blood by a method due to Pauli. The blood-serum, to which was added a

FIG. 6.



small quantity of toluene to prevent putrefaction, was placed in small parchment cells suspended in closed glass vessels filled with distilled water. The serum was dialysed for six weeks against distilled water saturated with toluene. During the first three weeks the water was changed daily, thereafter every second day. The

concentration of the solutions was determined as in the case of solutions of egg-albumen.

TABLE 9.—*Solubility of Carbon Dioxide in Solutions of Serum-Albumen* (see also Fig. 5).

Concentration: 0.44 gram of albumen in 100 c.c. of solution.

Density=0.998.

Pressure	748	844	945	1089	1246	1415
Solubility ..	0.804	0.800	0.802	0.804	0.806	0.806

Concentration: 1.29 grams in 100 c.c. of solution. Density=1.000.

Pressure	744	838	966	1066	1261	1431
Solubility	0.779	0.774	0.778	0.785	0.789	0.792

The influence of concentration on the solubility at atmospheric pressure is shown in Fig. 7.

(i) *Silicic Acid.*

Solutions of silicic acid were prepared by dissolving pure silica in potassium hydroxide and adding excess of hydrochloric acid. The liquid was then dialysed, first against tap water, and then against distilled water, until free from chloride.

TABLE 10.—*Solubility of Carbon Dioxide in Solutions of Silicic Acid.*

Concentration: 1.40 grams of SiO_2 in 100 c.c. of solution.

Density=1.000.

Pressure	731	829	936	1064	1193	1354
Solubility	0.822	0.819	0.816	0.816	0.816	0.816

Concentration: 2.20 grams in 100 c.c. of solution. Density=1.002.

Pressure	732	836	938	1038	1178	1335
Solubility	0.828	0.822	0.820	0.820	0.820	0.820

Concentration: 2.80 grams in 100 c.c. of solution. Density=1.003.

Pressure	731	873	960	1050	1203	1380
Solubility	0.831	0.825	0.824	0.823	0.824	0.825

In this case the solubility-pressure curves are similar in form to those for carbon dioxide and ferric hydroxide (Fig. 1).

The influence of concentration on the solubility at atmospheric pressure is shown in Fig. 7.

(j) *Suspensions of Charcoal and of Silica.*

Suspensions of Kahlbaum's well-powdered bone charcoal and of pure silica were employed. The solubility of carbon dioxide in presence of such suspensions is given in the following table:

TABLE II. (See Fig. 6).

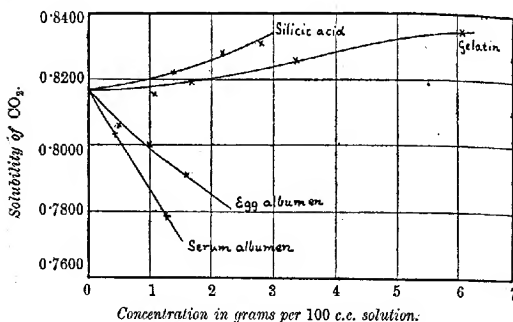
0.236 gram of charcoal in 100 c.c. Density = 1.000.

Pressure	748	812	909	1069	1160	1250	1372
Solubility	0.815	0.823	0.845	0.892	0.919	0.940	0.950

0.253 gram of silica in 100 c.c. Density = 1.000.

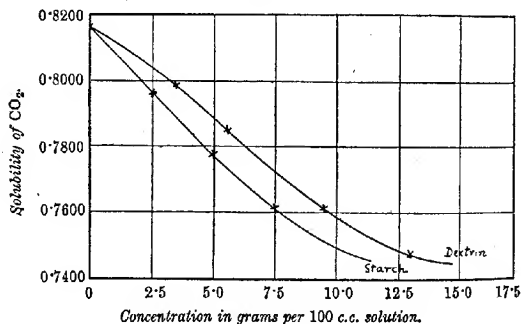
Pressure	748	849	962	1048	1182	1274	1359
Solubility	0.814	0.815	0.818	0.819	0.821	0.822	0.824

FIG. 7.



In the case of charcoal suspensions, the initial comparatively rapid absorption of gas was followed by a comparatively slow

FIG. 8.



absorption lasting from six to ten hours. The solubility values given in the above table are calculated from the maximum volume

of gas absorbed by the liquid. In the case of silica suspensions, the liquid quickly became saturated with the carbon dioxide, no slow absorption being observed.

II.—Solubility of Nitrous Oxide.

The nitrous oxide was prepared by heating pure ammonium nitrate in a flask at about 210–225°. Before the heat was applied, the flask was thoroughly exhausted. When the pressure of nitrous oxide in the apparatus had become equal to atmospheric pressure (a manometer was attached to the apparatus), a certain amount of the gas was allowed to escape into the air. The outlet to the air was then closed, and the nitrous oxide caused to bubble through solutions of potassium hydroxide and ferrous sulphate before being stored in a gasholder filled with brine. Before being used, it was dried by means of calcium chloride and phosphoric oxide. The solubility of the nitrous oxide in water, and in water containing colloids and suspensions, was then determined in exactly the same manner as with carbon dioxide. The following tables contain the results obtained.

TABLE 12.—Solubility of Nitrous Oxide in Water.

Pressure	758	842	967	1041	1185	1382
Solubility	0.592	0.593	0.592	0.593	0.592	0.592
Pressure	758	831	997	1082	1214	1361
Solubility	0.592	0.593	0.592	0.593	0.594	0.592
Pressure	758	889	971	1091	1190	1281
Solubility	0.591	0.592	0.591	0.592	0.593	0.593

From these and other similar determinations, the mean value of the solubility of nitrous oxide in water was found to be 0.592, the solubility being independent of the pressure within the limits investigated.

TABLE 13.—Solubility of Nitrous Oxide in Ferric Hydroxide Solutions (see also Fig. 9).

Concentration: 0.625 gram of $\text{Fe}(\text{OH})_3$ in 100 c.c. of solution.
Density=1.001.

Pressure	758	846	934	1010	1121	1383
Solubility	0.590	0.586	0.584	0.588	0.588	0.588

Concentration: 1.49 grams in 100 c.c. of solution. Density=1.008.

Pressure	734	828	935	1078	1215	1432
Solubility	0.586	0.579	0.577	0.581	0.585	0.586

Concentration: 4.061 grams in 100 c.c. of solution. Density=1.029.

Pressure	754	835	838	1093	1208	1358
Solubility	0.578	0.573	0.571	0.574	0.579	0.580

Contrary to the behaviour of carbon dioxide, the solubility of nitrous oxide is lowered by ferric hydroxide, the diminution of solubility being practically proportional to the concentration, as shown in Fig. 14. Further, the behaviour of nitrous oxide is unlike that of carbon dioxide, in that there is no long period of slow absorption observable, neither at high nor at low pressures.

FIG. 9.

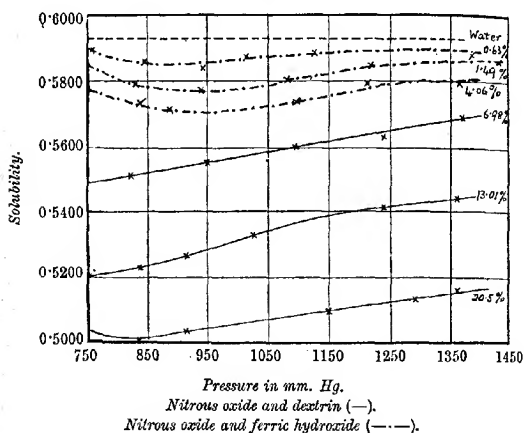


TABLE 14.—*Solubility of Nitrous Oxide in Solutions of Dextrin*
(see also Fig. 9).

Concentration: 6.98 grams of dextrin in 100 c.c. of solution.
Density=1.018.

Pressure	739	822	949	1092	1239	1368
Solubility	0.549	0.550	0.556	0.560	0.562	0.569

Concentration: 13.01 grams in 100 c.c. of solution. Density=1.039.

Pressure	729	836	914	1023	1237	1358
Solubility	0.529	0.523	0.526	0.533	0.540	0.544

Concentration: 20.30 grams in 100 c.c. of solution. Density=1.062.

Pressure	740	836	911	1149	1290	1360
Solubility	0.503	0.499	0.503	0.509	0.513	0.516

Compare also Fig. 15.

TABLE 15.—*Solubility of Nitrous Oxide in Solutions of Arsenious Sulphide.*

Concentration: 1·85 grams of As_2S_3 in 100 c.c. of solution.
Density = 1·004.

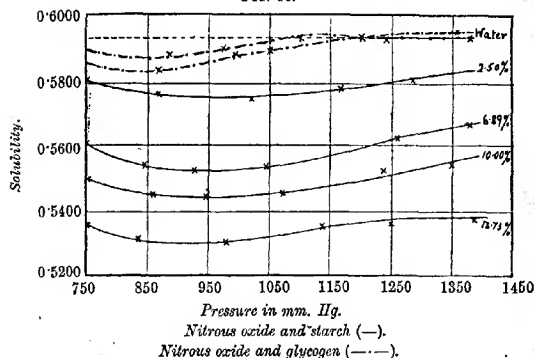
Pressure	746	820	924	1055	1196	1346
Solubility	0·591	0·590	0·590	0·592	0·593	0·593

Concentration: 2·29 grams in 100 c.c. of solution. Density = 1·007.

Pressure	746	850	1006	1110	1209	1300
Solubility	0·590	0·586	0·588	0·589	0·589	0·590

From these figures it is seen that arsenious sulphide is without influence on the solubility of nitrous oxide.

FIG. 10.

TABLE 16.—*Solubility of Nitrous Oxide in Solutions of Starch*
(see also Fig. 10).

Concentration: 2·50 grams of starch in 100 c.c. of solution.
Density = 1·009.

Pressure	742	871	1020	1166	1284	1441
Solubility	0·580	0·576	0·575	0·578	0·581	0·582

Concentration: 6·89 grams in 100 c.c. of solution. Density = 1·021.

Pressure	742	848	929	1046	1261	1381
Solubility	0·561	0·554	0·553	0·554	0·562	0·567

Concentration: 10·00 grams in 100 c.c. of solution. Density = 1·030.

Pressure	742	860	943	1071	1239	1350
Solubility	0·550	0·544	0·545	0·545	0·553	0·555

Concentration: 13·73 grams in 100 c.c. of solution. Density = 1·040.

Pressure	739	836	982	1136	1252	1387
Solubility	0·537	0·532	0·530	0·535	0·536	0·538

The influence of concentration on the solubility is shown in Fig. 15.

TABLE 17.—*Solubility of Nitrous Oxide in Solutions of Gelatin*
(see also Fig. 11).

Concentration: 1.31 grams of gelatin in 100 c.c. of solution.
Density = 0.999.

Pressure	731	849	937	1069	1176	1328
Solubility	0.589	0.590	0.590	0.592	0.592	0.592

Concentration: 3.09 grams in 100 c.c. of solution. Density = 1.003.

Pressure	730	858	950	1089	1230	1373
Solubility	0.581	0.582	0.584	0.586	0.588	0.588

Concentration: 6.06 grams in 100 c.c. of solution. Density = 1.008.

Pressure	730	850	961	1097	1247	1379
Solubility	0.560	0.563	0.566	0.568	0.570	0.571

The influence of concentration of gelatin on the solubility shown in Fig. 14.

FIG. 11.

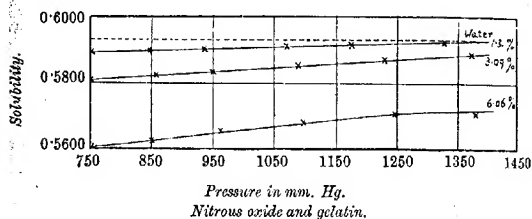


TABLE 18.—*Solubility of Nitrous Oxide in Solutions of Glycogen*
(see Fig. 10).

Concentration: 0.49 gram of glycogen in 100 c.c. of solution.
Density = 0.999.

Pressure	738	889	977	1102	1239	1386
Solubility	0.590	0.588	0.591	0.594	0.594	0.594

Concentration: 1.00 gram of glycogen in 100 c.c. of solution.
Density = 1.002.

Pressure	737	871	991	1050	1201	1360
Solubility	0.585	0.584	0.589	0.591	0.594	0.596

The influence of concentration of glycogen on the solubility of nitrous oxide is shown in Fig. 14.

TABLE 19.—*Solubility of Nitrous Oxide in Solutions of Egg-Albumen* (see also Fig. 12).

Concentration: 0.35 gram of albumen in 100 c.c. of solution.

Density=0.998.

Pressure	735	830	954	1139	1249	1363
Solubility	0.580	0.578	0.580	0.581	0.580	0.580

Concentration: 0.75 gram in 100 c.c. of solution. Density=1.000

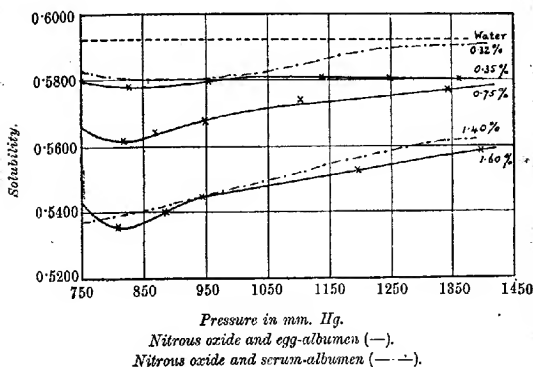
Pressure	735	820	872	951	1104	1344
Solubility	0.569	0.562	0.564	0.567	0.573	0.577

Concentration: 1.60 grams in 100 c.c. of solution. Density=1.005

Pressure	729	811	886	946	1199	1399
Solubility	0.548	0.535	0.540	0.544	0.553	0.558

The influence of concentration on solubility is shown in Fig. 14

FIG. 12.

TABLE 20.—*Solubility of Nitrous Oxide in Solutions of Serum Albumen* (see also Fig. 12).

Concentration: 0.32 gram of serum-albumen in 100 c.c.

Density=0.998.

Pressure	746	873	978	1126	1259	1395
Solubility	0.583	0.581	0.579	0.586	0.588	0.591

Concentration: 1.40 grams in 100 c.c. of solution. Density=1.001

Pressure	748	842	913	1048	1223	1388
Solubility	0.537	0.533	0.545	0.550	0.558	0.562

The influence of concentration on solubility is shown in Fig. 14.

TABLE 21.—*Solubility of Nitrous Oxide in Solutions of Silicic Acid*
(see also Fig. 13).Concentration: 1.87 grams of SiO_2 in 100 c.c. of solution.
Density = 1.001.

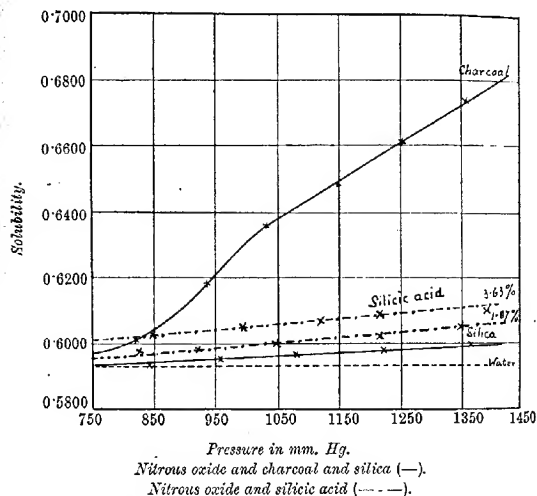
Pressure	748	825	921	1046	1217	1349
Solubility	0.596	0.598	0.598	0.600	0.602	0.604

Concentration: 3.63 grams in 100 c.c. of solution. Density = 1.005.

Pressure	741	848	994	1122	1217	1394
Solubility	0.601	0.602	0.605	0.607	0.608	0.609

The influence of concentration on the solubility is shown in
Fig. 14.

FIG. 13.

TABLE 22.—*Solubility of Nitrous Oxide in Water containing Charcoal and Silica in Suspension* (see also Fig. 13).

100 c.c. of liquid contained 0.227 gram of charcoal. Density = 1.000.

Pressure	729	824	938	1034	1150	1254	1356
Solubility	0.596	0.600	0.618	0.635	0.648	0.661	0.674

100 c.c. of liquid contained 0.30 gram of SiO_2 . Density = 1.000.

Pressure	730	846	960	1081	1224	1365	1481
Solubility	0.592	0.593	0.595	0.597	0.597	0.600	0.602

III.—*Solubility of Carbon Dioxide in Solutions of Aniline.*

In order that the solubility curves previously obtained might be compared directly with a case where chemical combination is known to occur, the solubility of carbon dioxide in solutions of aniline was determined. The results are contained in table 23.

FIG. 14.

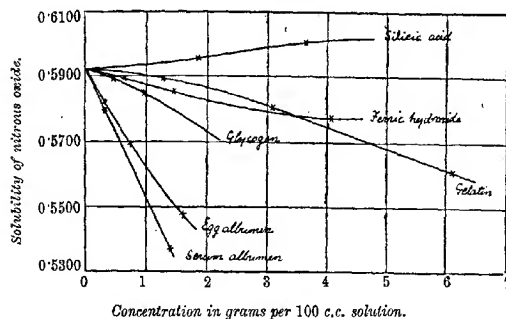


TABLE 23.

Concentration: 0.206 gram of aniline in 100 c.c. of solution.

Pressure	748	808	920	1053	1159	1243
Solubility	0.865	0.855	0.857	0.855	0.862	0.860

Concentration: 0.425 gram in 100 c.c. of solution.

Pressure	760	816	921	1150	1236	1380
Solubility	0.909	0.897	0.897	0.897	0.902	0.908

Concentration: 0.566 gram in 100 c.c. of solution.

Pressure	760	823	941	1082	1223	1341
Solubility	0.935	0.929	0.925	0.923	0.924	0.930

Concentration: 0.743 gram in 100 c.c. of solution.

Pressure	760	895	983	1063	1223	1302
Solubility	0.953	0.941	0.940	0.940	0.940	0.942

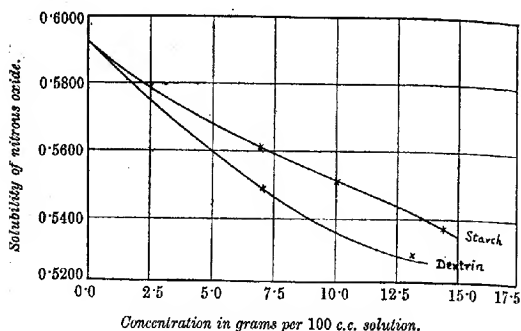
The solubility-pressure curves are similar in form to those for carbon dioxide and ferric hydroxide (Fig. 1).

IV.—*Solubility of Carbon Dioxide in Solutions of Potassium Chloride.*

Although many investigators (see Steiner, *Annalen*, 1894, 52, 275; Gordon, *Zeitsch. physikal. Chem.*, 1895, 18, 1; Braun, *ibid.*,

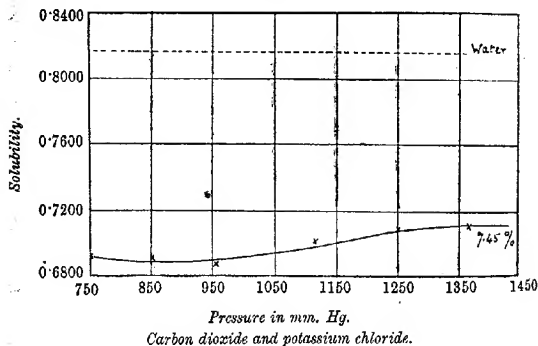
556 FINDLAY AND CREIGHTON: THE INFLUENCE OF COLLOIDS AND
 1900, 33, 721; Knapp, *ibid.*, 1904, 48, 39; Turner, *ibid.*, 1907,
 57, 611) have studied the influence of dissolved substances, both
 electrolytes and non-electrolytes, on the solubility of gases, such

FIG. 15.



investigations have always been made at only one pressure. In
 order that a comparison might be made between the influence of
 colloids and suspensions (emulsoids and suspenoids) and of true

FIG. 16.



solutions, the solubility of carbon dioxide in solutions of potassium
 chloride at different pressures was determined. The results are
 contained in table 24, and represented in Fig. 16.

TABLE 24 (see also Fig. 16).

Concentration: 7.45 grams of KCl in 100 c.c. of solution.
Density = 1.043.

Pressure	756	850	953	1116	1249	1362
Solubility	0.694	0.693	0.688	0.700	0.709	0.710

Concentration: 5.00 grams of KCl in 100 c.c. Density = 1.031.

Pressure	756	832	901	1050	1150	1223
Solubility	0.731	0.727	0.724	0.726	0.735	0.736

Concentration: 2.56 grams of KCl in 100 c.c. Density = 1.016.

Pressure	756	852	981	1079	1190	1362
Solubility	0.767	0.761	0.761	0.762	0.768	0.766

Discussion of Results.

A glance at the curves given on the preceding pages will show that many peculiarities of behaviour are found in the solubility of gases in liquids when that solubility is investigated, not, as previously, at only one pressure, but at different pressures. So varied, indeed, is the influence, not only in degree, but in kind, of the different solutes or pseudo-solutes and suspensions on the solubility of carbon dioxide and nitrous oxide, that conclusions drawn from the behaviour under one pressure might be very erroneous when considered for another pressure.

The substances the influence of which on the solubility of the two gases, carbon dioxide and nitrous oxide, has been studied, may be divided into emulsoids and suspensoids. To the former class belong ferric hydroxide, gelatin, starch, glycogen, egg-albumen, serum-albumen, and silicic acid; to the latter class, arsenious sulphide, charcoal, and silica. Dextrin may, perhaps, be regarded as intermediate between a true solute and an emulsoid. Aniline and potassium chloride have been included merely for the purposes of comparison.

In the case of the emulsoids, we see that *under atmospheric pressure*, silicic acid increases the solubility both of carbon dioxide and of nitrous oxide; ferric hydroxide and gelatin increase the solubility of carbon dioxide but diminish the solubility of nitrous oxide; and the other emulsoids decrease the solubility of both the gases. Of the suspensoids, arsenious sulphide is practically without influence on the solubility of either gas, while charcoal and silica increase the solubility of both gases. Lastly, dextrin decreases the solubility of both carbon dioxide and of nitrous oxide.

What the nature of the interaction may be in the case of gelatin and carbon dioxide is not, perhaps, quite easily decided.

Gelatin, as is known, is an amphoteric substance, and may therefore function as a weak base. It seems to us, however, to be doubtful if this basic property is sufficient in itself to explain the whole increase in the solubility. Possibly some more complicated action occurs, an indication of which appears to be given by the effect of carbon dioxide in lowering the gelatinisation point of gelatin solutions already referred to (p. 544).

In the case of ferric hydroxide, as has already been pointed out by Luther and Krsnjavi (*Zeitsch. physikal. Chem.*, 1905, **46**, 170), there is probably complex ion formation. The formation of a ferric carbonate appears from the work of Raikow (*Chem. Zeit.*, 1907, **31**, 87) and of Cameron and Robinson (*J. Physical Chem.*, 1908, **12**, 561) to be excluded.

Although in these cases we may regard chemical combination as being one of the causes, perhaps the main cause, of the increased solubility of carbon dioxide, it is difficult to adopt a similar explanation in the case of silicic acid, which increases the solubility both of carbon dioxide and of nitrous oxide. In the latter case an explanation is more probably to be sought in the phenomena of adsorption (see also p. 560).

Solubility Referred to the Water in the Solutions.—With regard to the lowering effect of electrolytes and non-electrolytes on the solubility of gases in water, the view has been expressed, more especially by J. C. Philip (*Trans.*, 1907, **91**, 711), that the observed depression can be explained on the assumptions: (1) that only the water in the solution acts as solvent for the gas, and that this solvent power is not affected by the presence of the solute; (2) that the solute molecules are more or less hydrated, and therefore diminish the amount of active solvent for the gas; (3) that the gas does not dissolve in the solute, whether anhydrous or hydrated.

It must be borne in mind that the cases investigated by us are not generally comparable with those to which Philip applied his theory, for with the exceptions of the solutions of potassium chloride, and, possibly, dextrin, the solvent systems were not homogeneous, but must be regarded, most probably, as heterogeneous. And that alters the case entirely.

With regard to the solutions of potassium chloride, it may be mentioned that the values calculated for the degree of hydration vary from 6.42 to 8.68 molecules of water to one molecule of salt. These numbers are rather lower than those calculated by Philip, but not greatly so.

In the case of dextrin, however, it is evident that the solutions of dextrin show considerably different behaviour, according as the solubility of carbon dioxide or of nitrous oxide is investigated.

In the former case practically no hydration is evidenced; in the latter case a slight amount of hydration would be calculated. But in the case of carbon dioxide it will be seen that the numbers representing the solubility referred to water in the solution diminish with increase of concentration, whereas in the case of nitrous oxide, the numbers increase.

It does not appear to us that sufficient evidence has yet been adduced in support of the theory put forward by Philip. Moreover, we believe that the solubility curves which we have obtained at higher pressures show the necessity of extending the range of investigation in this direction. On this we are at present engaged.*

Change of Solubility with Pressure.—Whatever conclusions may be drawn as regards the influence of the suspensoids and emulsoids on the solubility of carbon dioxide and nitrous oxide from determinations at one pressure, they must to a greater or lesser degree be found inaccurate when applied over a range of pressures; for as the figures previously given show, the solubility is not independent of the pressure (as it is in the case of pure water), nor are the solubility curves for solutions of different concentration in all cases parallel.

Assuming that the influence of ferric hydroxide and of gelatin is mainly due to chemical combination with formation of a largely hydrolysed compound, we should expect that the solubility-pressure curve would first fall, owing to hydrolysis, and then remain nearly horizontal, owing to the diminution of hydrolysis by addition of carbonic acid. This is the type of curve obtained with aniline and ferric hydroxide, but is better seen in the case of the more weakly basic substance gelatin. Looked at in this way, the curve for carbon dioxide and silicic acid would also indicate chemical combination, and we should therefore have to assume that silicic acid is amphoteric (for which we do not know of any other evidence), or that between silicic acid and carbonic acid a reaction takes place comparable with that between silicic acid and hydrofluoric acid, the compound formed being highly hydrolysed.

As regards the influence of suspensions of charcoal and silica on the solubility of carbon dioxide and nitrous oxide, and of silicic acid on the solubility of nitrous oxide, it will be noticed that we are here dealing with curves similar to those obtained by other investigators for the absorption of gases or of dissolved substances by charcoal.

* Since this was written, a paper has appeared (this vol., p. 66) by F. L. Usher, who fails to find confirmation of the theory put forward by Philip.

Similarity is also shown by the fact that when one examines the relation between the concentration of gas in the water and in the solid, the general relationship $c_2/c_1 = \text{const.}$ found by previous workers for "adsorption" phenomena, also holds in the present cases. Here c_2 is the weight of gas taken up by the water in 100 c.c. of the suspension, and c_1 the weight taken up by the suspended solid. x we have found to be equal to 4.

TABLE 25.

Charcoal and Carbon Dioxide, 0.236 gram of Charcoal in 100 c.c.				Charcoal and Nitrous Oxide, 0.227 gram of Charcoal in 100 c.c.			
Pressure.	c_1 .	c_2 .	c_2^4/c_1 .	Pressure.	c_1 .	c_2 .	c_2^4/c_1 .
950	0.0086	0.1837	0.132	950	0.0059	0.1332	0.053
1000	0.0127	0.1934	0.110	1000	0.0085	0.1402	0.048
1050	0.0178	0.2030	0.099	1050	0.0109	0.1472	0.043
1150	0.0266	0.2224	0.092	1150	0.0151	0.1613	0.045
1250	0.0365	0.2417	0.098	1250	0.0200	0.1753	0.047
1350	0.0430	0.2610	0.108	1350	0.0259	0.1893	0.050

In the above cases, therefore, increased solubility would be ascribed to "adsorption," accompanied or unaccompanied by absorption.

The solubility curves so far discussed are comparatively simple in form, and the influence of the colloid or suspension may plausibly be explained on the basis of partial chemical combination or of "adsorption," accompanied or unaccompanied by absorption. In these cases the solubility of the gases is increased at all pressures.

In most of the cases examined, however, where dealing with emulsoids, the solubility of the gas is diminished even when one takes into account the volume of water in the solution. This may be explained, formally, by the assumption of hydrate formation. But even if this be accepted, the remarkable behaviour observed at higher pressures remains to be accounted for. An examination of the solubility-pressure curves shows that, with the exception of the cases already discussed, there exists for a number of the colloids a very well-defined minimum of solubility, this minimum being more marked in concentrated than in dilute solutions. In all such cases the influence of the colloid must be a very complex one, and two effects at least must enter into play, one causing a diminution of solubility with pressure, the other an increase. In dilute solutions the former is sometimes absent or negligible.

What are these two factors? So far as the rising portion of the curves is concerned, we assume that the rise is due to "adsorption," whatever the true nature of this process may be. For this portion of the different curves we have also found that the ratio $c_2/c_1 = \text{const.}$, as is shown by the following table:

TABLE 26.

Serum-Albumen and Nitrous oxide.

1.40 grams of albumen per 100 c.c.

Pressure.	c_1 .	c_2 .	c_2/c_1 .
915	0.0017	0.1164	0.108
1000	0.0026	0.1272	0.100
1050	0.0031	0.1336	0.103
1150	0.0047	0.1463	0.098
1250	0.0061	0.1590	0.105
1350	0.0079	0.1717	0.111

0.537 is the value of the solubility used for calculating c_2 .

A similar degree of constancy is obtained in the case of the other curves.

As regards the factor producing the lowering of the solubility, we believe that the simplest assumption to make is that of solubility of the gas in the colloid phase. As has already been pointed out, we are dealing here with heterogeneous systems, comparable with a mixture of two partly miscible liquids. So far as we are aware, the solubility of a gas in such a system has not yet been investigated; but we may very properly assume that the gas dissolves (unequally) in the two phases, namely, in the cases under discussion, in the aqueous phase and the colloid phase. We must also further assume that the solubility in the colloid phase no longer follows Henry's law, but that the solubility increases less rapidly than the pressure. Under such conditions the solubility curve would no longer be a straight line, but would fall with increase of pressure. Such a deviation from Henry's law signifies that the molecular weight of the gas in the gaseous phase and in the colloid phase is no longer the same; and we must therefore assume that the gases have a higher molecular weight in the colloid phase than in the water phase. That is, we must assume polymerisation of the gas in the colloid phase. By these assumptions we are enabled to explain, formally at least, the behaviour observed, and it must be left to future investigation to show whether the explanation is only formal or may be regarded as essential. It is clear, however, from the foregoing investigation that colloids in solution will not necessarily increase the solubility of a gas. The action is a specific one, and depends both on the colloid and on the gas.

CHEMICAL DEPARTMENT.

UNIVERSITY OF BIRMINGHAM.

LVIII.—*Absorption Spectra and Melting-point Curves of Aromatic Diazoamines.*

By CLARENCE SMITH and CONSTANCE HAMILTON WATTS.

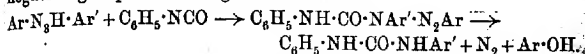
THE discovery by Griess that the same diazoamine is formed by diazotising either of two primary aromatic amines and coupling the product with the other, led twenty or thirty years ago to numerous investigations which had for their object the determination of the constitution of such mixed diazoamines and the isolation of the two possible isomeric forms, $\text{ArN}_2\cdot\text{NHAr}'$ and $\text{ArNH}\cdot\text{N}_2\text{Ar}'$. The latter purpose has never been satisfactorily realised, whilst the former has resulted in a mass of such conflicting evidence that even at the present time the constitution of the aromatic diazoamines remains an open question.

In order to show that the conclusions at which we have arrived are supported by the bulk of this earlier evidence, it is necessary to recapitulate the main points made by previous investigators, the more so as an impartial survey of all the facts appears to have been omitted hitherto.

An examination of the substances obtained by decomposing with water the product of the action of carbonyl chloride on a benzene solution of a diazoamine led Sarauw to the conclusion that the imino-group is attached to the more negative aromatic nucleus, and that the initial product (not isolated) of the reaction is a diazo-carbamide, $\text{ArN}_2\cdot\text{NAr}'\cdot\text{CO}\cdot\text{NAr}'\cdot\text{N}_2\text{Ar}$, in which Ar is the less negative benzenoid group. A perusal of the author's two papers (*Ber.*, 1881, 14, 2442; 1882, 15, 42) proves, however, that his evidence is inconclusive, for whilst phenol and dibromocarbaniide are the products arising from the decomposition by water of the diazo-carbamide obtained from benzenediazoamino-*p*-bromobenzene, the action of water on the diazo-carbamide from benzenediazoamino-*p*-toluene yields both phenol and *p*-cresol and a viscous product from which only di-*p*-tolylcarbamide can be isolated. The viscous product may and probably does contain diphenylcarbamide, seeing that both phenol and *p*-cresol are formed. If such is the case, the diazoamine reacts with carbonyl chloride in accordance with both formulæ, $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{NH}\cdot\text{C}_7\text{H}_7$, and $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{N}_2\cdot\text{C}_7\text{H}_7$. Similar reasoning holds in the case of benzenediazo-*m*-aminobenzoic acid, phenol and *m*-hydroxybenzoic acid being the only substances isolated from the decomposition products of its diazo-carbamide.

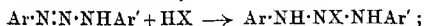
The preceding constitution of a mixed diazoamine has been far more satisfactorily established by Goldschmidt and Molinari (*Ber.*,

1888, 21, 2578), by heating equimolecular quantities of the diazoamine and phenylcarbimide in an indifferent solvent, such as benzene. The product is a diazocarbamide, which can be isolated and appears to be an individual substance; it is decomposed by water, yielding a phenol, nitrogen, and a diarylcarbamide, of which one aromatic group is always phenyl, and the other the more negative group of the original diazoamine:



In the preceding year, however, the results of two investigations were published which partly supported and partly opposed Goldschmidt's conclusions. Heumann and Oeconomides (*Ber.*, 1887, 20, 372, 904) found that diazoaminobenzene, when heated in phenol, reacted to form aniline and benzeneazophenol; similarly, *p*-chlorobenzenediazoamino-*p*-toluene gave *p*-chloroaniline and *p*-tolueneazophenol. Benzenediazoamino-*p*-toluene, however, with phenol or resorcinol gave approximately equal quantities of aniline and *p*-toluidine and a mixture of hydroxyazo-compounds. In these reactions, therefore, some mixed diazoamines behave as if constituted in accordance with Goldschmidt's formula, others like mixtures of equal quantities of $\text{Ar}\cdot\text{N}_2\cdot\text{NHAr}'$ and $\text{Ar}\cdot\text{NH}\cdot\text{N}_2\cdot\text{Ar}'$. Still more striking is the evidence advanced by Noeling and Binder (*Ber.*, 1887, 20, 3004), who submitted benzenediazoamino-*p*-toluene and other mixed diazoamines to the attack of numerous reagents, and found that they behaved sometimes in accordance with the formula $\text{Ar}\cdot\text{N}_2\cdot\text{NHAr}'$, sometimes in accordance with the formula $\text{Ar}\cdot\text{NH}\cdot\text{N}_2\cdot\text{Ar}'$, but generally as a mixture of both forms.

As a result of these and other investigations, two views were current regarding the constitution of mixed aromatic diazoamines, and these have not been materially modified by more recent researches. One view, which does not appear to have been urgently advanced by any single investigator, regards the mixed diazoamines as consisting of the two possible isomerides, $\text{Ar}\cdot\text{N}_2\cdot\text{NHAr}'$ and $\text{Ar}\cdot\text{NH}\cdot\text{N}_2\cdot\text{Ar}'$. The other theory, initiated by Goldschmidt, regards the diazoamines as being constituted so that the imino-group is attached to the more negative aromatic group. Reactions in which the diazoamine yields four products of decomposition are attributed to a migration of the iminic hydrogen atom due to the presence of water, alcohol, or an electrolyte, and are explained by an initial addition of water or the like; thus:

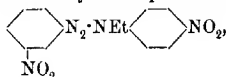


by the elimination of HX, $\text{Ar}\cdot\text{NH}\cdot\text{N}_2\cdot\text{Ar}'$ and $\text{Ar}\cdot\text{N}_2\cdot\text{NHAr}'$ may result, and by subsequent decomposition yield each a pair of products. Goldschmidt claimed that the migration of the iminic

hydrogen atom does not occur in indifferent solvents, such as benzene, petroleum, or chloroform, and consequently in such solvents diazoamines behave as individual substances and not as mixtures, and to this cause attributes the success of his phenylcarbimide method of determining the constitution of diazoamines.

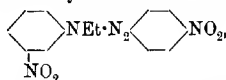
In arriving at this theory, Goldschmidt apparently has overlooked the exhaustive researches in 1886—1895 of Meldola and Streatfeild on alkylated diazoamines. Although alkylation as a method of determining constitution has been viewed in recent years with some suspicion, yet in some instances, for example, the phthaleins and the hydroxyazo-compounds, the problem of the constitution of a substance containing a mobile hydrogen atom has been approached and to a great extent solved by replacing the migratory hydrogen atom by an immobile alkyl group. If, therefore, an alkylated diazoamine can be shown to have a similar constitution to that of its parent substance, Meldola and Streatfeild's researches acquire a new and fundamental significance, and can be utilised directly to prove the untenability of the theory that in a mixed aromatic diazoamine the imino-group is attached to the more negative aromatic nucleus. We have been able to prove the point in question by means of the spectrograph. Meldola and Streatfeild showed that three isomeric *mp'*-dinitrodiazoethylaminobenzenes exist, namely:

I. *m*-Nitrobenzenediazoethylamino-*p*-nitrobenzene,



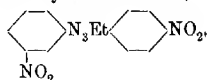
prepared from diazotised *m*-nitroaniline and *p*-nitroethylaniline.

II. *p*-Nitrobenzenediazoethylamino-*m*-nitrobenzene,



from diazotised *p*-nitroaniline and *m*-nitroethylaniline.

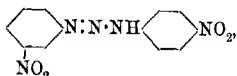
III. *mp'*-Dinitrodiazoethylaminobenzene,



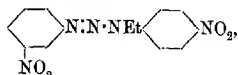
obtained by the direct ethylation of *mp'*-dinitrodiazoaminobenzene.

Isomeride III gives an absorption curve different from those of I and II, and absolutely identical with that of its parent diazoamine, which is thus proved to have a constitution similar to that of isomeride III. The constitution of this isomeride has been practically proved by Meldola and Streatfeild, who find that it can be

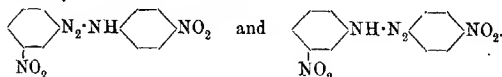
synthesised by heating equimolecular quantities of isomerides I and II in alcohol or benzene. Meldola and Streatfeild regard III as a compound of I and II. For reasons given below we believe it to be an equimolecular mixture of I and II, but for the present purpose this difference of opinion is immaterial, the main point being that III is composed of equal quantities of I and II, either mixed or combined. Now, in the diazoamine under discussion, the *p*-nitrobenzene nucleus is probably the more negative, but whether this is really so does not affect the argument. Assuming that it is, the diazoamine will be represented by the Goldschmidt theory by the formula:



and the directly alkylated derivative, which must possess a similar constitution to that of its parent substance from the spectrometric evidence, will have the formula:



that is, should be identical with isomeride I above. Since experiment shows that the directly alkylated derivative is III above, that is, a mixture of equal quantities of I and II, it follows that the premise is incorrect, and that *mp'*-dinitrodiazoaminobenzene consists of a mixture (or compound) of equal quantities of the two individually unknown isomerides:



Of course, the acceptance of this theory at once renders intelligible the numerous reactions in which a mixed diazoamine yields four products of decomposition. It only remains to explain why the diazoamine at times yields only two products, decomposing as though it consisted entirely of one of the two unknown isomerides. At present it is impossible to advance any argument satisfactorily supported by experimental evidence. The most obvious explanation is the selective attack of the reagent. If one of the two isomerides is attacked at a much greater rate than the other, a transformation of the less susceptible into the more susceptible isomeride must occur in order to preserve the equilibrium ratio at unity, and the diazoamine will decompose almost entirely as though it consisted of one isomeride only. The most important case to which this explanation can be applied is the phenylcarbimide reaction, since

this forms the main foundation of the Goldschmidt theory of the constitution of diazoamines. Goldschmidt attributes the formation of an individual diazocarbamide from phenylcarbimide and a mixed diazoamine in benzene solution to the immobility of the iminic hydrogen atom in an indifferent solvent. Dimroth, however, gives instances (*Annalen*, 1904, **335**, 1) in which the transformation of one tautomeride into another by the migration of a mobile hydrogen atom proceeds much more rapidly in an indifferent solvent than in a hydroxylic solvent. Goldschmidt admits that this is correct in principle, but is not applicable to the particular case of the diazoamines, because one of the isomeric forms is unknown (*Ber.*, 1906, **38**, 1097). Our experiments prove, however, that both forms exist as an inseparable mixture in the mixed diazoamine. The unitary course of the phenylcarbimide reaction, therefore, may very well be due to the selective attack of the reagent, the transformation of one isomeride in the mixed diazoamine into the more susceptible form being facilitated by the indifferent solvent to such a degree that one diazocarbamide is produced only in inappreciable quantities.

It would be premature to dogmatise from the result of the examination of a single triplet of ethers originating from a diazoamine containing aryl groups of not very different character, and we do not unhesitatingly commit ourselves at present to the views advanced above, and the less so in consequence of Pechmann's work on amidines of the type $\text{ArN}:\text{CPh}\cdot\text{NH}\cdot\text{Ar}'$ (*Ber.*, 1895, **28**, 869), which differ from mixed diazoamines by containing the group CPh in place of a nitrogen atom. The compound $\text{C}_6\text{H}_5\cdot\text{N}:\text{CPh}\cdot\text{NH}\cdot\text{C}_2\text{H}_5$, obtained from benzanilide iminochloride and *p*-toluidine, is identical with $\text{C}_7\text{H}_7\cdot\text{N}:\text{CPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$, prepared from benzoyl-*p*-toluidide iminochloride and aniline, but yields by ethylation a mixture of two ethyl derivatives corresponding with the two formulæ given. When Ar and Ar' are different in character, however, the amidines produced by the two methods are still identical, but yield only one ether, indicating an immobility of the hydrogen atom in the amidine. A similar constitution may obtain for mixed diazoamines containing aryl groups of very different character, the imino-group remaining attached to the negative nucleus as in the Goldschmidt theory. This view of the constitution of such diazoamines, which, of course, harmonises well with the chemical behaviour cited above, can be tested spectrometrically, and is receiving our attention.

The derivative obtained by the direct alkylation of a mixed diazoamine has been shown by Meldola and Streatfeild to be composed of equal quantities of the two isomerides, $\text{ArN}_2\cdot\text{NR}\cdot\text{Ar}'$ and $\text{ArNR}\cdot\text{N}_2\cdot\text{Ar}'$, by boiling an alcoholic or benzene solution of

these isomerides for one hour, whereby a product is obtained identical with the directly alkylated diazoamines. The authors regard this product as a compound of the two isomerides, although they found that the molecular weight in benzene by the cryoscopic method agreed with a unimolecular and not a bimolecular formula, a discrepancy which they attribute to dissociation of the compound in the benzene solution. This explanation is untenable, since the compound is produced in boiling benzene, and it is very improbable that it would dissociate in the cold solvent. Mr. T. J. Mander, to whom we proffer our thanks, has determined the molecular weights of several alkylated mixed diazoamines in boiling alcohol and benzene, and has obtained values which are always less than those corresponding with the unimolecular formula. The compound, therefore, does not exist in the solution, and must be produced, if formed at all, at the instant of the deposition of the solid from the solution. To ascertain whether or not a compound is formed, we have determined the melting-point curve of mixtures of *p*-nitrobenzenediazoethylamino-*m*-nitrobenzene and *m*-nitrobenzenediazoethylamino-*p*-nitrobenzene. The curve is of the simple U-shape characteristic of mixtures, and has its minimum at a point corresponding with the mixture of equal quantities of the two isomerides and a temperature identical with the melting point of the substance obtained by the direct ethylation of *mp*-dinitrodiazoaminobenzene. This evidence, combined with that furnished by the cryoscopic and the ebullioscopic methods of determining the molecular weight, proves that the directly ethylated substance is a solid solution of equal quantities of the two isomerides mentioned above.

EXPERIMENTAL.

mp-Dinitrodiazoaminobenzene.—This compound was prepared in the usual way from *m*-nitroaniline and *p*-nitrobenzenediazonium chloride in the presence of sodium acetate. The crude substance melted at 214°; after crystallisation from a mixture of equal volumes of alcohol and toluene, the melting point was 218–219°. Since Meldola and Streatfeild give the melting point as 212–212.5° (Trans., 1889, 55, 416), the substance was again dissolved in boiling alcohol and toluene, filtered while still hot (precipitate A), again when cold (precipitate B), and yet again after concentrating the mother liquor (precipitate C). The melting points of A, B, C respectively were 220°, 212.5–213°, 219–220°. After recrystallisation from the same solvent, the melting points were 231–232°, 231–232°, 230–231°, in a bath previously heated to 180°. After a third recrystallisation, the melting points were 231–232°, 231–232°, 228°. In all cases the substance decomposes

at the melting point. The three samples all gave the same orange-red colour in alcoholic sodium hydroxide, and dissolved without change of colour in concentrated sulphuric acid, forming solutions which ultimately became colourless. The melting point of *pp'*-dinitrodiazoaminobenzene is given by Hantzsch as 233° (decomp.), a value which we have confirmed. The melting point of a mixture of approximately equal quantities of this compound and our *mp'*-isomeride melted at 208—211° (decomp.).

mp'-Dinitrodiazoethylaminobenzene was prepared by heating the diazoamine with alcoholic potassium hydroxide and ethyl iodide on the water-bath for eight hours, and twice recrystallising the product from alcohol. It melted at 152—153°, dissolved in alcoholic sodium hydroxide without change of colour, and gave a solution in concentrated sulphuric acid, which became colourless after a few hours.

m-Nitrobenzenediazoethylamino-*p*-nitrobenzene and *p*-nitrobenzenediazoethylamino-*m*-nitrobenzene were prepared from diazotised *m*-nitroaniline and *p*-nitroethylaniline and diazotised *p*-nitroaniline and *m*-nitroethylaniline respectively, and were recrystallised from alcohol and toluene until the melting points were constant at 174.5—174.8° and 188.5—188.7° respectively; the substances dissolved in alcoholic sodium hydroxide without change of colour, and gave solutions in concentrated sulphuric acid, which ultimately became colourless.

The absorption curves of *mp'*-dinitrodiazoaminobenzene and of the three ethylated isomerides are shown in Fig. 1. The curves of the parent diazoamine and of its directly ethylated derivative are identical throughout. The curves of the other two isomerides, although naturally very similar to, are quite distinct from, that of the directly ethylated isomeride. A comparison of the three curves, particularly in the neighbourhood of oscillation frequencies 3200 to 3600, indicates that the curve of the directly ethylated diazoamine is very much what would be expected if the substance is a mixture of the other two isomerides. The most important result, however, is the proof of the similarity of the constitutions of *mp'*-dinitrodiazoaminobenzene and its directly ethylated derivative.

To obtain the melting-point curve of *m*-nitrobenzenediazoethylamino-*p*-nitrobenzene and *p*-nitrobenzenediazoethylamino-*m*-nitrobenzene shown in Fig. 2, it is necessary that the heating of the different mixtures shall be as uniform and under as nearly the same conditions as possible, for it is well known that the apparent melting point of a diazoamine can be raised many degrees by rapid heating. Intimate mixtures of the two isomerides were obtained by making two solutions in benzene distilled over sodium:

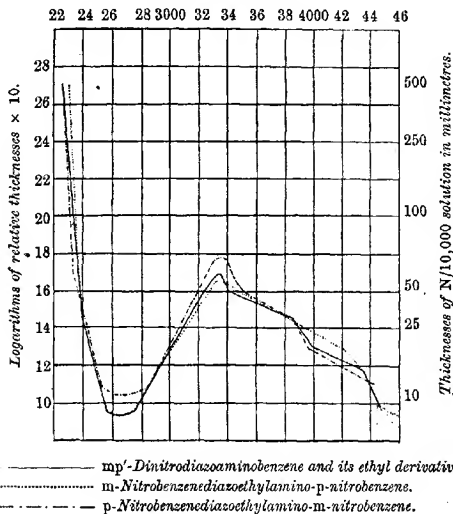
A. Containing 0.1575 gram of *m*-nitrobenzenediazoethylamino-*p*-nitrobenzene in 250 c.c.

B. Containing 0.1575 gram of *p*-nitrobenzenediazoethylamino-*m*-nitrobenzene in 250 c.c.

Mixtures of different volumes of these two solutions were evaporated on the water-bath, the residue was detached from the basin, finely powdered, and transferred as completely as possible to capillary tubes about 2 mm. in diameter and about 15 cm. long.

FIG. 1.

Oscillation frequencies.

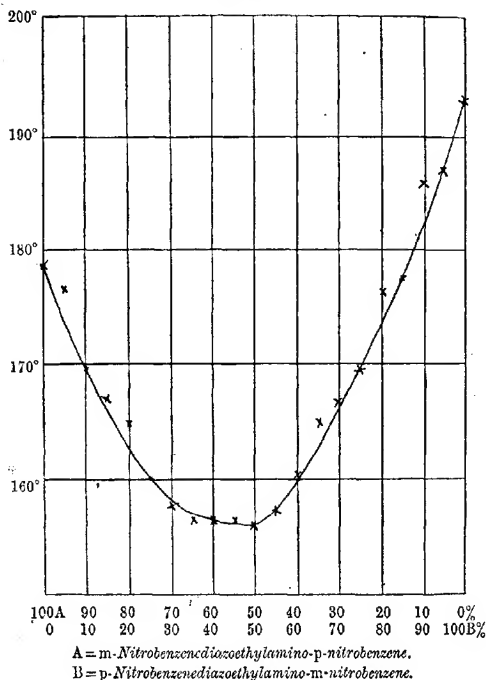


These tubes were attached to a thermometer 70 cm. in length, having a range from 100° to 200° , graduated in tenths of a degree. The bulb of the thermometer was immersed in sulphuric acid contained in the outer jacket of a Victor Meyer vapour density apparatus. The temperature of the acid was raised to 100° , then the capillary tube was affixed to the thermometer, and the temperature was raised fairly rapidly to within 10° of the melting point of the preceding mixture; the rate of heating was then adjusted so that the temperature rose 1° per minute.

The following table gives the data from which the curve in Fig. 2 is plotted:

C.c. of A.	C.c. of B.	Corrected melting point.	C.c. of A.	C.c. of B.	Corrected melting point.
20	0	178.5—178.8°	9	11	157.2°
19	1	176.6	8	12	160.2—161.6
18	2	169.1—169.8	7	13	164.5—165.5
17	3	166.9—167.2	6	14	166.8—167.4
16	4	164.5—165.4	5	15	169.1—169.8
15	5	169.6—160.4	4	16	176.1—176.9
14	6	157.3—157.5	3	17	177.6—177.9
13	7	156.1—156.5	2	18	185.9—186.1
12	8	156.4—156.9	1	19	186.9—187.2
11	9	156.3—156.9	0	20	198.2—193.4
10	10	155.4—156.2			

FIG. 2.



It will be noticed that mixtures containing from 65 to 50 per cent. of A melt at only slightly different temperatures, but there

is not the slightest doubt that the equimolecular 50 per cent. mixture has the lowest melting point, which is the same as that of the substance obtained by the ethylation of *mp'*-dinitrodiazoaminobenzene.

In order to see whether a compound of the two isomerides is formed under the conditions mentioned by Meldola and Streatfeild, mixtures of A and B were heated under a reflux condenser for one hour on the water-bath; the benzene was then evaporated, and the melting points of the residues determined as above. The results tabulated below show that the melting points are practically unchanged by this treatment:

C.c. of A.	C.c. of B.	Corrected melting point.	C.c. of A.	C.c. of B.	Corrected melting point.
20	0	178.2—178.3°	8	12	160.4—160.9°
15	5	159.3—159.7	5	15	168.8—169.8
12	8	156.3—156.8	0	20	192.0—192.6
10	10	155.1—155.7			

In conclusion, we wish to express our thanks to the Research Fund Committee of the Chemical Society for a grant by which the expense of this investigation has been largely defrayed.

EAST LONDON COLLEGE.

LIX.—*The Relation between Absorption Spectra and Chemical Constitution. Part XIV. The Aromatic Nitro-compounds and the Quinonoid Theory.*

By EDWARD CHARLES CYRIL BALY, WILLIAM BRADSHAW TUCK, and EFFIE GWENDOLINE MARSDEN.

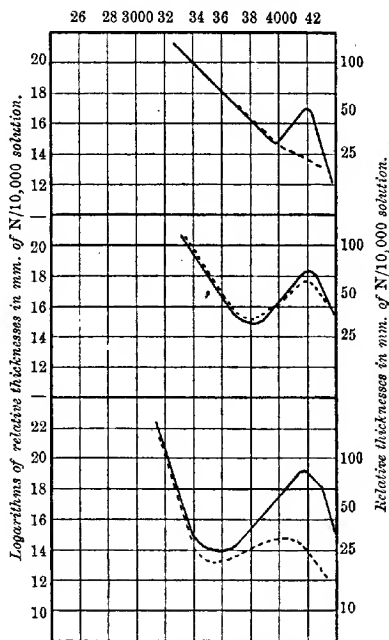
It has been shown (Trans., 1905, 87, 1332) that the introduction of the nitro-group into the benzene nucleus produces a very marked effect on the absorption spectrum, for, whereas the parent hydrocarbon shows a number of closely situated absorption bands, nitrobenzene is characterised by a very strongly marked general absorption with only a very shallow band.* The view was put forward that this change is due to the fact that the strong residual affinity of the nitro-group restrains the vibrations of the benzene ring. If, now, a second group be introduced, and this group be of the so-called positive type, that is to say, one with directing influence to the ortho- and para-positions, the tendency of the nitro-group to restrain the benzene ring vibrations is more or less eliminated.

* The presence of this shallow band has only recently been detected with a large spectrograph in the case of an alcoholic solution. Nitrobenzene in petroleum solution does not show the band.

We have now examined a number of aromatic compounds derived from nitrobenzene, and we find that these substances all show more or less pronounced absorption bands, the depth and position

FIG. 1.

Oscillation frequencies.



Upper curves	<i>o</i> -Nitrotoluene	{ full curve $N/1000$ dotted „ $N/10,000$
Middle „	<i>m</i> -Nitrotoluene	{ full curve $N/1000$ dotted „ $N/10,000$
Lower „	<i>p</i> -Nitrotoluene	{ full curve $N/1000$ dotted „ $N/10,000$

of which depend on the character of the substituent group or groups.

The simplest cases are those of the three nitrotoluenes, where the second group is the not very strongly marked electropositive methyl. The absorption curves of the ortho-, meta-, and para-isomerides are shown in Fig. 1 (full curves), and they all three

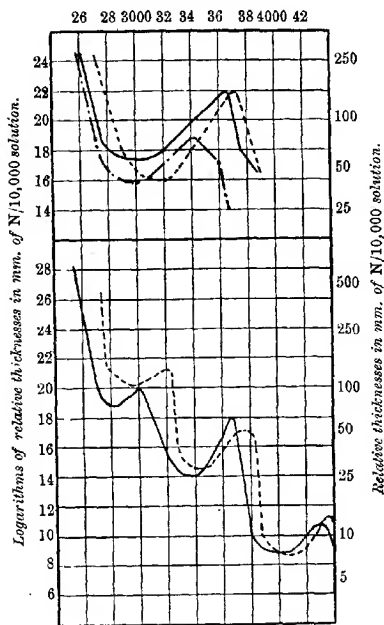
show well-marked absorption bands. The differences between the absorption as shown by the full and dotted curves will be discussed below under the section dealing with the effect of the solvent. The

FIG. 2.

Upper Curves.

Full curve *α-Nitronaphthalene in alcohol.*
Dotted curve " " *light petroleum.*
Dot and dash curve " " *benzene.*

Oscillation frequencies.



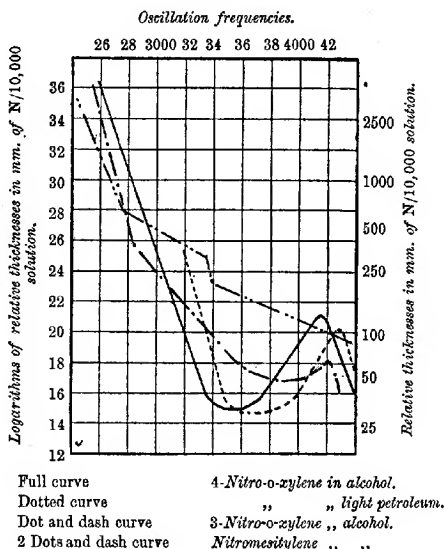
Lower Curves.

Full curve *β-Nitronaphthalene in alcohol.*
Dotted curve " " *light petroleum.*

two mononitronaphthalenes also show well-marked absorption bands, as can be seen on reference to the full curves in Fig. 2. The α -compound shows one band, whilst the β -isomeride has three. We

have also examined the absorption of the two mononitro-*o*-xylenes, the curves being shown in Fig. 3. Here again well-marked bands are exhibited. It is noticeable in a comparison of 4-nitro-*o*-xylene with the nitrotoluenes that the former compound possesses a much deeper band than the latter. Clearly, therefore, the two methyl groups in the former substance exert a greater counteracting influence against the restraint of the nitro-group than the single methyl group in the nitrotoluenes. At the same time, the relative position of the nitro-group and the methyl groups has a considerable

FIG. 3.



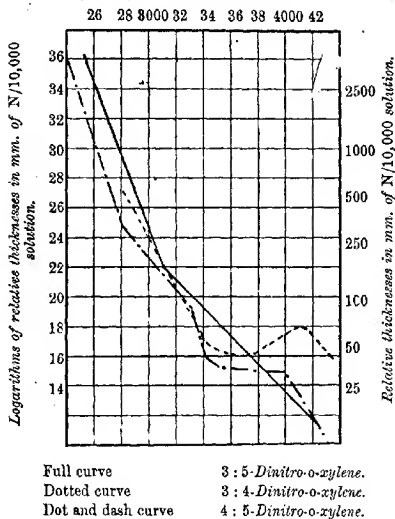
bearing on their mutual influence. Thus, in the nitrotoluenes the *ortho*-isomeride shows an absorption which is the shallowest and farthest from the red, whilst the band of the *para*-isomeride is the deepest and nearest the red. The small band given by 3-nitro-*o*-xylene is therefore attributable to the fact that the two methyl groups and the nitro-group are adjacent to one another. This is still more strikingly exemplified in the case of nitromesitylene, which shows no band at all. This follows readily from the fact that the three methyl groups are all in the *meta*-positions with

respect to one another; as has been previously shown, mesitylene exhibits very small absorption owing to this fact, and therefore the three methyl groups will not be able to overcome the restraint of the nitro-group, because they of themselves also tend to restrain the vibrations of the ring.

In the case of the two nitronaphthalenes the restraining influence of the nitro-group on the one ring is eliminated by the second ring, with the result that very well-marked absorption bands are produced which are nearer the red than those of naphthalene itself. In both

FIG. 4.

Oscillation frequencies.



these compounds, especially in the α -isomeride, the absorption bands are sufficiently near to the red for the substances to be visibly coloured.

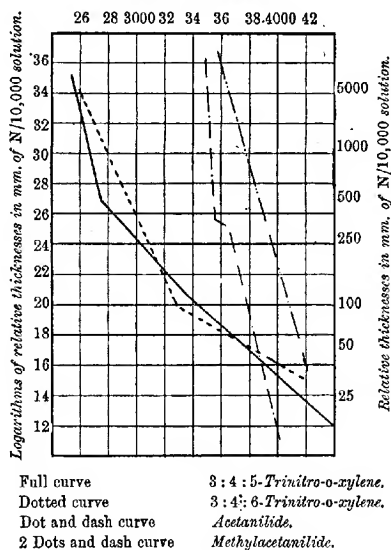
If two nitro-groups are substituted in one benzene ring, then of course the influence of the positive groups must be greater in order to produce a counteracting effect equal to that in a mono-nitro-compound. This is well shown in the case of the two dinitro-o-xylenes (Fig. 4), of which the 3:4-dinitro-isomeride shows a very shallow band, whilst in the 4:5-dinitro-isomeride the

absorption band has just disappeared. Still more pronounced is this the case in trinitro-compounds, for both the 3:4:5- and the 3:4:6-trinitro-*o*-xylenes (Fig. 5) show only general absorption without even the attempt to show the band evidenced by the 4:5-dinitro-compound.

The definite conclusion can therefore be drawn that if the restraining influence of the nitro-group in nitrobenzene is counteracted by the introduction of one or more so-called positive groups,

FIG. 5.

Oscillation frequencies.



isotropism is set up, and one or more absorption bands are produced. Further, the position and persistence of this absorption are determined by the amount that the restraining influence of the nitro-group is eliminated as a result of the introduction of the positive groups, and also by the position of the absorption band of the non-nitrated compound.

As a further test, the spectra of mono- and di-nitrofluorene were examined. The first of these (I) is practically colourless, having only a slight cream colour, while the dinitro-compound (II) is

strongly yellow. These two compounds afford a rigid test of the above conclusion, for the mononitro-compound should show a

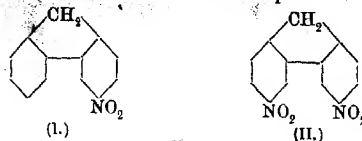
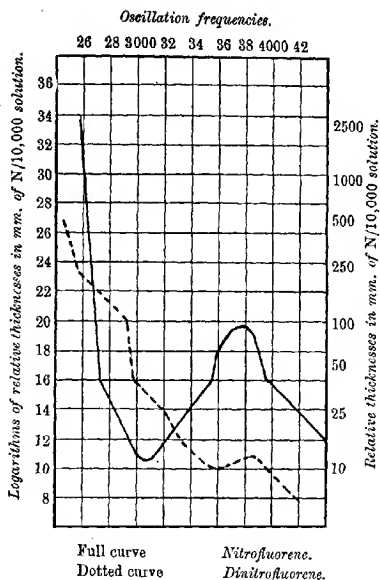


FIG. 6.



strong absorption band, whilst the dinitro-compound should show very little or no evidence of a band, since both phenyl groups have their motions restrained by a nitro-group. The curves are shown in Fig. 6, and, as can be seen, the results are exactly as was predicted.

We have also examined the absorption spectra of nitrobenzene substituted by other groups than methyl, as, for example, the nitrocinnamic ethyl esters. Their absorption curves are shown in Fig. 7, and here there is a deep absorption band at $1/\lambda = 3350$ in the para-isomeride. The meta-compound shows a band at $1/\lambda = 3850$, and a step-out at $1/\lambda = 3200$, whilst the ortho-isomeride

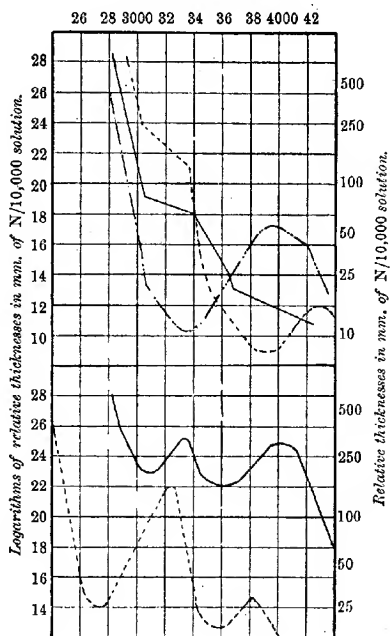
only shows a step-out at $\lambda = 3200$. There is also here a progressive effect of the $\cdot\text{CH}_2\text{CH}_2\text{CO}_2\text{Et}$ group from the ortho- to the para-position as in the nitrotoluenes.

FIG. 7.

Upper Curves.

Full curve	<i>o</i> -Nitrocinnamic ester.
Dotted curve	<i>m</i> -Nitrocinnamic ester.
2 Dots and dash curve	<i>p</i> -Nitrocinnamic ester.

Oscillation frequencies.



Lower curves.

Full curve	<i>o</i> -Coumaric acid in alcohol.
Dotted curve	<i>o</i> -Coumaric acid in alcoholic NaOEt.

If now the substituent group be very strongly positive, it is evident from what has gone before that the absorption band will tend to be nearer the red, for it must be remembered that the

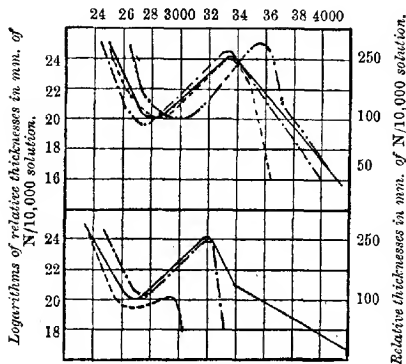
absorption band of benzene substituted by a strong positive group, such as OMe or OEt, is generally more persistent and nearer the red than that of the xylenes, or toluene. This is very strikingly observed in the case of nitroquinol dimethyl ether, the absorption of which in alcoholic solution is shown in Fig. 8. The head of the absorption band is now at $1/\lambda = 2800$, which is distinctly nearer the red than the compounds previously described. The

Fig. 8.

Upper Curves.

Full curve	<i>Nitroquinol dimethyl ether in alcohol.</i>	
Dotted curve	"	" benzene.
Dot and dash curve	"	" chloroform.
2-Dots and dash curve	"	" light petroleum

Oscillation frequencies.



Lower curves.

Full curve	<i>Nitroquinol dimethyl ether in water.</i>	
Dotted curve	"	" aniline.
Dot and dash curve	"	" pyridine.

compound, as is well known, has a strong yellow colour, and its solution in alcohol is also yellow. It is evident that the absorption of this compound, and therefore its colour, is capable of the same explanation as that put forward for the compounds previously described, that is to say, it is due to the isorropesis between the residual affinity of the nitro-group and that of the quinol dimethyl ether residue. The absorption spectrum of the quinol dimethyl ether has already been described (Trans., 1905, 87, 1353), and shows a very deep absorption band with its head at about $1/\lambda = 3445$.

The question now arises as to whether the above explanation of the absorption and colour of the substituted nitro-compounds should not be perfectly general and include all the substances of this type, such as the nitroanilines and the nitrophenols. In the last two classes of compounds the colour and absorption has been attributed to their existing in the quinonoid configuration. Indeed, one of us, in conjunction with Dr. Stewart and Dr. Edwards (Trans., 1906, 89, 514), put this forward as the interpretation of the results obtained from the spectroscopic observation of the nitrophenols and the nitroanilines. In the case of the former it was judged that the sodium salts have the quinonoid formula owing to their absorption bands being so much nearer to the red than those of the free substances. On the other hand, from the results described in this paper, it would seem more probable that another explanation of their absorption spectra is preferable, an explanation similar to that given above for the nitro-compounds, which clearly cannot exist in a simple quinonoid form. On these lines, the absorption bands of the nitroanilines, for example, would be due to the isorropesis between the nitro-group and the aniline residue. These bands would necessarily be very near the red owing to the fact that the absorption band of aniline is high up the spectrum ($1/\lambda=3500$). As regards the nitrophenols and their sodium salts there should be a considerable difference in their absorption on account of the great difference between the absorption of phenol and of sodium phenoxide. The absorption spectrum of phenol (Trans., 1905, 87, 1351) shows a band with its head at $1/\lambda=3680$, whilst sodium phenoxide shows a band with head at $1/\lambda=3420$. In nitrophenols, therefore, the isorropesis is between the free period of the nitro-group and a residue with bands at $1/\lambda=3680$, whilst in the sodium nitrophenoxides the isorropesis is between the nitro-group and a residue with a band at $1/\lambda=3420$. Clearly, therefore, the absorption of the latter compound should be much nearer the red.

We thought it worth while, therefore, to undertake anew the investigation of these compounds with the help of the new and much better spectrograph than was available at the time of the previous investigation. We will deal first with the nitroanilines and their alkyl derivatives. In Fig. 9 are shown the curves of 3-nitro-*p*-toluidine, its mono- and di-methyl, and also the acetyl and acetylmethyl derivatives. The free base shows a deep absorption band with its head at about $1/\lambda=2400$, the mono-methyl derivative a band with head at $1/\lambda=2350$, whilst the head of the dimethyl compound lies at $1/\lambda=2270$. While it may be urged that the absorption of the free base and the monomethyl derivative is due to their existing in the quinonoid form, it is

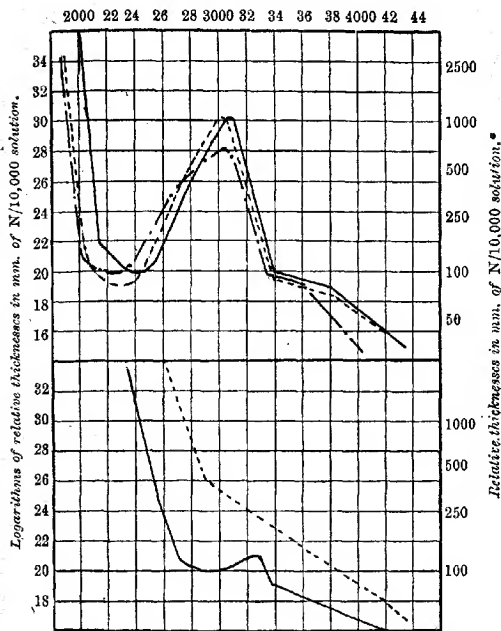
difficult to see how the dimethyl compound can exist in this form, and yet the absorption of all three is almost identical. The only

FIG. 9.

Upper curves.

Full curve	<i>Nitro-p-toluidine.</i>
Dotted curve	<i>Nitromethyl-p-toluidine.</i>
Dot and dash curve	<i>Nitrodimethyl-p-toluidine.</i>

Oscillation frequencies.



Lower curves.

Full curve	<i>Nitroaceto-p-toluidide.</i>
Dotted curve	<i>Nitromethylaceto-p-toluidide.</i>

ifference between them is the slight shift of the band towards the red accompanying the introduction of the methyl groups. In connexion with this, it is important to note that the band of

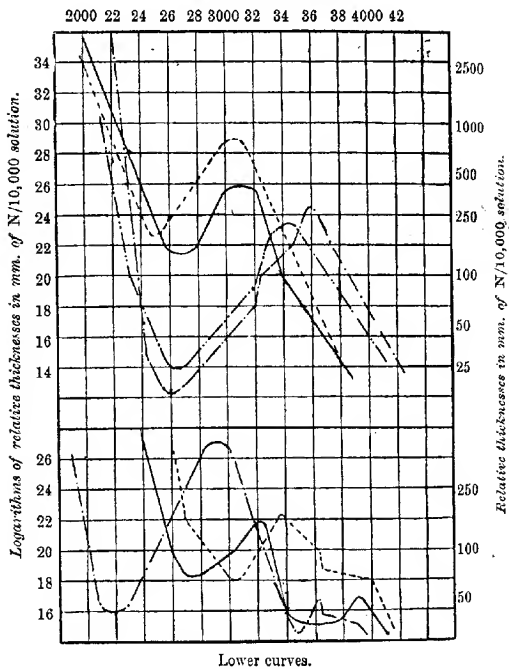
aniline also shifts towards the red when the substance is methylated. The heads of the bands of aniline, methylaniline, and

Fig. 10.

Upper curves.

Full curve	<i>m</i> -Nitroaniline.
Dotted curve	<i>m</i> -Nitrodimethylaniline.
Dot and dash curve	<i>p</i> -Nitroaniline.
2-Dots and dash curve	<i>p</i> -Nitrodimethylaniline.

Oscillation frequencies.



Lower curves.

Full curve	<i>Nitro-p-cresol</i> in alcohol.
Dotted curve	<i>Nitro-p-cresetole</i> in alcohol.
Dot and dash curve	<i>Nitro-p-cresol</i> in alcoholic NaOEt.

dimethylaniline lie at $1/\lambda = 3510, 3450, \text{ and } 3430$ respectively. It follows that the bands of the nitro-compound will also shift when the latter is methylated.

The reduction in the absorption arising from the decrease in the residual affinity of the amino-group caused by the introduction of the acetyl group and the acetyl and methyl groups is well shown in the two remaining curves. This is exactly analogous to the decrease in the absorption of aniline caused by the introduction of the acetyl group and the acetyl and methyl groups, as shown by the curves in Fig. 5.

The absorption of *m*- and *p*-nitroanilines compared with that of their dimethyl derivatives is shown in Fig. 10. Exactly the same applies here as in the case of the *o*-nitroamino-compound just described. There is no difference of any moment between the free compounds and the dimethyl derivatives. The conclusion, therefore, is forced upon us that the same explanation of the colour and absorption must be given in each. A simple quinonoid structure is ruled out in the case of the dimethyl compounds, and hence we are compelled to abandon it in the case of the parent substances.

As regards the nitrophenols, the same explanation without doubt is applicable to the para-isomeride as to the compounds already described, for whilst *p*-nitrophenol and *p*-nitroanisole have the same absorption (the bands of anisole and phenol are in the same spectral region), the band of sodium *p*-nitrophenoxide is shifted considerably towards the red. This shift, however, is due to the shift in the absorption band towards the red when sodium hydroxide is added to a phenol solution. In the case of the *o*-nitrophenols, however, the matter is complicated by the fact that in the original paper the spectrum of *o*-nitroanisole differed from that of *o*-nitrophenol.

In order to elucidate this anomaly, we have examined the spectra of *o*-nitrophenol, *o*-nitroanisole, and *o*-nitrophenetole in various solvents, and find that the difference is mainly due to the effect of the solvent. As previously referred to, the influence of the solvent is very remarkable in the case of the nitro-compounds, and this influence will be discussed more fully below. In the original paper, *o*-nitrophenol was shown to have two bands; these are shown in the full curve in Fig. 11, which represents the absorption of an alcoholic solution of this compound. The solution in light petroleum, however, only shows one band—the one nearer the red, whilst the second band has shrunk to a step-out. *o*-Nitroanisole in light petroleum solution also shows one absorption band like the parent substance in the same solvent, but a little nearer the shorter wave-lengths. In alcoholic solution *o*-nitroanisole only shows evidences of the one band nearer the red. This band is shallow, and was only detected with the new instrument. *o*-Nitro-

phenetole shows the same shallow band and also a step-out where the second band should appear.

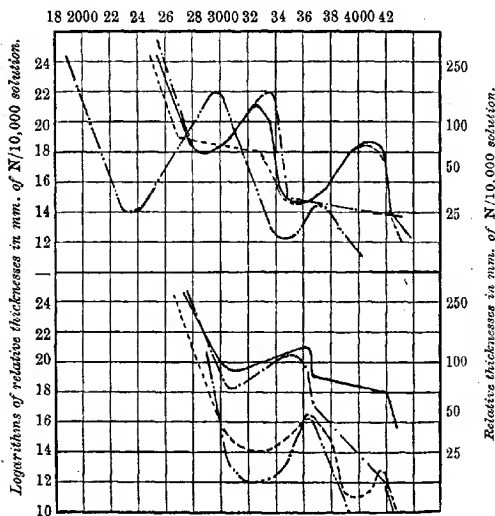
The solution of *o*-nitrophenol in water is different, for the band nearer the red has shrunk to a step-out, whilst the other band is

FIG. 11.

Upper curves.

Full curve	<i>o</i> -Nitrophenol in alcohol.
Dotted curve	" " water.
Dot and dash curve	" " light petroleum.
2-Dots and dash curve	" " alcoholic NaOEt.

Oscillation frequencies.



Lower curves.

Full curve	<i>o</i> -Nitroanisole in alcohol.
Dotted curve	" " light petroleum.
Dot and dash curve	" " alcohol.
2-Dots and dash curve	" " light petroleum.

well marked. Now, *o*-nitrophenol in aqueous solution of the strength dealt with ($N/1000$) is presumably considerably ionised, and, further, this ionisation must be less in alcoholic solution and negligible in light petroleum solution. It would seem from this and

from a comparison with the curves of the ethers that the ionisation of the nitrophenol causes the band nearer the red to shrink, while in the non-ionised substance this band is well marked, while the band farther from the red is decreased.

The absorption of sodium *o*-nitrophenoxide is given in Fig. 11, and shows the first band well marked and the second band very shallow. The change in the absorption when the parent substance is converted into its sodium salt is simply a shift of both absorption bands nearer to the red. As was pointed out above, a shift of this character is bound to take place, because the absorption band of phenol also undergoes a similar shift when sodium hydroxide is added to the solution. The explanation of the absorption of the nitrotoluenes and other compounds advanced above meets this case equally well, and there seems absolutely no reason to assume a radical change in structure such as quinonoid formation in order to explain this shift in the absorption without any change in the type.

Now, owing to the presence of a considerable excess of sodium ethoxide in the solution, it is very improbable that the sodium *o*-nitrophenoxide is ionised to any considerable extent. This is in agreement with the observations, because the ionised or partly ionised nitrophenol in water shows a tendency on the part of the longer wave-length absorption band to shrink, whilst the second band is well marked, the reverse effect being produced when the nitrophenol is dissolved in light petroleum. The sodium salt (in presence of excess of sodium ethoxide in alcoholic solution) is analogous to the latter case, for the shorter wave-length band is decreased, while the other is relatively very deep.

In order not to base our conclusions on one single *o*-nitrophenol we have examined also *m*-nitro-*p*-cresol and its ethyl ether (Fig. 10) and the results are identical with those of *o*-nitrophenol. The *m*-nitro-*p*-cresetole shows a band at $1/\lambda = 3050$ and a step-out at about $1/\lambda = 3850$; the parent substance in alcohol shows the first band at $1/\lambda = 2800$, and the second band at $1/\lambda = 3650$, whilst in the presence of sodium ethoxide the two bands are shifted to $1/\lambda = 2200$ and $1/\lambda = 3500$ respectively. In aqueous solution the absorption is quite analogous to the case of *o*-nitrophenol, for the shorter wave-length band is increased in persistence, whilst the other one is decreased to a step-out.

We have also repeated the original examination of *m*-nitrophenol and compared it with *m*-nitrophenetole. As the curves on Fig. 12 show, the relation between the free compound, its sodium salt, and its ethyl ether is the same as in the case of the ortho-isomeride, and the same explanation holds good. The para-compounds have

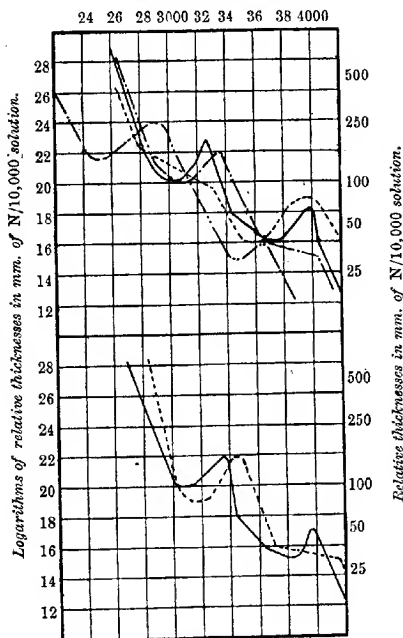
also been examined, and their absorption curves are shown in Fig. 13. Exactly the same shifts of the absorption bands may

FIG. 12.

Upper curves.

Full curve	<i>m</i> -Nitrophenol in alcohol.
Dotted curve	" " water.
Dot and dash curve	" " light petroleum.
2 Dots and dash curve	" " alcoholic NaOEt

Oscillation frequencies.



Lower curves.

Full curve	<i>m</i> -Nitrophenol in alcohol.
Dotted curve	" " light petroleum.

here, the only difference being that one deep band is exhibited in the place of the two in the *o*- and *m*-isomerides.

An interesting point may be mentioned here in reference to the

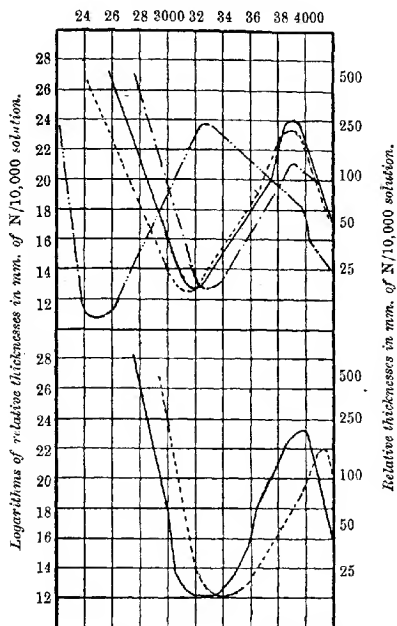
amino- and the ONa groups. It appears from the absorption of aniline and sodium phenoxide that the residual affinity of these

Fig. 13.

Upper curves.

Full curve	<i>p</i> -Nitrophenol in alcohol.
Dotted curve	" " water.
Dot and dash curve	" " light petroleum.
2 Dots and dash curve	" " alcoholic NaOEt.

Oscillation frequencies.



Lower curves.

Full curve	<i>p</i> -Nitrophenolate in alcohol.
Dotted curve	" " light petroleum.

two groups is very nearly the same, for the heads of the bands of the two compounds are in the same position. The analogy between these two groups has often been noticed by us in comparing the

spectra of compounds containing first one and then the other group. The resemblance between the nitroanilines and the corresponding sodium nitrophenoxides is very striking.

Perhaps one of the most important arguments against a quinonoid configuration for the nitroanilines and nitrophenols is to be found in the fact that the absorption bands of all the compounds described in this paper appear at the same concentration of solution. This is the case whether the compound can or cannot exist in a quinonoid form. It must be remembered that the absorption spectrum of *p*-benzoquinone shows its isorropesis band at a concentration of $N/10$, whilst all the nitro-compounds show their bands in $N/1000$ -solution. Moreover, the shape of the absorption curve of quinone and those of the nitro-compounds is quite different. It therefore seems in the highest degree improbable that the shift in the absorption bands, which takes place without any change of type when the nitrophenols are converted into their sodium salts, is due to a radical change of structure, as is demanded by the quinonoid hypothesis. As collateral evidence it may be pointed out that the sodium salts of the nitrophenols are extremely similar in their absorption to the nitroanilines, and these again to their dimethyl derivatives. The latter cannot be written in a simple quinonoid form, and therefore the conclusion follows that none are in the quinonoid form.

If the theory put forward in this paper is correct, it is evident that it must be applicable to all the compounds obtained by substituting a positive group into benzaldehyde, benzoic acid, and acetophenone, for the $\cdot\text{CHO}$, $\cdot\text{CO}_2\text{H}$, and $\cdot\text{COMe}$ groups are quite analogous to the nitro-group in that they tend to restrain the motions of the benzene ring. Many such compounds have been examined, and some have been previously published (aminoacetophenones, aminobenzaldehydes), and the results of the investigation are analogous to those given above for the nitro-compounds.

Similarly, of course, the same explanation must be applicable to compounds derived from benzene by the substitution of a hydroxyl group and any other group which carries residual affinity. For example, in coumaric acid, where the group $\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$ is in the ortho-position with respect to the hydroxyl groups, absorption bands should appear, which should shift towards the red on the addition of an excess of sodium hydroxide. The curves obtained both with and without alkali are shown in Fig. 7, and, as can be seen, the free acid shows two absorption bands, which are shifted towards the red in strongly alkaline solution. In cinnamic acid, where the isorropesis takes place between the residual affinities of the phenyl group and the unsaturated side-chain, the absorption

band has its head at $1/\lambda = 3600$. In *o*-hydroxycinnamic acid there are two bands with heads at $1/\lambda = 3100$ and 3650, whilst in the disodium compound the two bands have their heads at $1/\lambda = 2750$ and 3600. The shift of the bands in the latter is sufficiently large for the substance to be strongly yellow. It is true that in the case of coumaric acid a quinonoid formula can be written, but there is considerable inherent improbability of this change taking place, for it necessitates the postulation of there being a greater attraction between sodium and carbon than between sodium and oxygen. On the other hand, the shift in the absorption when phenol is converted into sodium phenoxide is sufficient to cause the shift when the substituted compound is so treated. A striking analogy between the amino- and ONa groups is to be found in the fact that the coumaric acid in strongly alkaline solution fluoresces with the same yellowish-green colour as *o*-aminocinnamic acid.

There seems therefore to be very strong evidence against a quinonoid explanation of the absorption and colour of the nitrophenols and nitroanilines. It would seem, indeed, that this theory is quite unnecessary. The explanation advanced in this paper, an explanation based on the play of forces between the residual affinities in the various intramolecular groups, has the great advantage in that it embraces all the disubstituted benzene compounds with two dissimilar substituents whether or no a quinonoid configuration is possible. This explanation satisfies all the facts that have been observed, which the quinonoid theory does not, as, for example, the very small change in the absorption when a nitroaniline is methylated, and that the formula of a true quinone (*p*-benzoquinone) is of an absolutely different type.

We have also investigated the mononitro-derivatives of benzylideneaniline. These compounds are interesting, for when the nitro-group is substituted in the benzene residue a simple quinonoid structure is possible, but in the isomeric benzylidenenitroanilines this is not the case. A comparison of the absorption of these compounds shows that they are all strikingly similar, there being, however, slightly more marked absorption bands in the benzylidenenitroanilines than in the nitrobenzylideneanilines, that is to say, those compounds which can exist in the quinonoid form show rather less marked absorption than those which cannot do so. It appears to us that these substances afford very strong evidence against the quinonoid hypothesis. The absorption curves compared with that of benzylideneaniline itself are shown in Fig. 14.

During the progress of this investigation a very interesting paper has appeared by Buttle and Hewitt (*Trans.*, 1909, 95, 1755), in which the constitution of the di- and tri-nitrophenols is discussed.

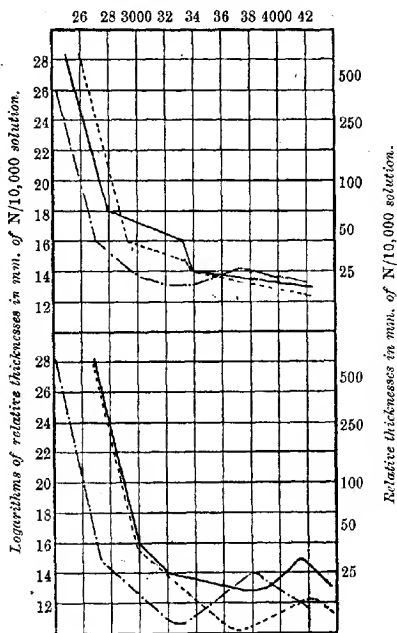
Buttle and Hewitt, basing their arguments largely on the results obtained in the original paper (Trans., 1906, 89, 514), attribute a para-quinonoid structure rather than an ortho-one to the sodium

FIG 14.

Upper curves.

Full curve	<i>o</i> -Nitrobenzylideneaniline.
Dotted curve	<i>m</i> -Nitrobenzylideneaniline.
Dot and dash curve	<i>p</i> -Nitrobenzylideneaniline.

Oscillation frequencies.



Lower curves.

Full curve	Benzylideneaniline.
Dotted curve	Benzylidene- <i>m</i> -nitroaniline.
Dot and dash curve	Benzylidene- <i>p</i> -nitroaniline.

salt of 2:4-dinitrophenol. On the other hand, there is another interpretation to be given to their results, and one which is more satisfactory than the one they give.

In the first place, Buttle and Hewitt assume that the absorption spectra of the ionised di- and tri-nitrophenols would be those of the *aci*-forms of these compounds. This, however, is not the case as far as the ortho-nitrophenol is concerned, and it would seem worth while that the absorption spectra of these substances in aqueous solution should be examined. It appears from the curves of the two dinitrophenols that there is evidence of a second band at about $1/\lambda = 3900$, which renders the compounds similar to *o*-nitrophenol itself. We would therefore expect the aqueous solution to show this second band more fully developed at the expense of the first band. Again, our results with the solutions of the nitrophenols in light petroleum solution show that the spectrum of the non-ionised compound can be readily obtained in this way. There is no doubt also that considerable importance is to be derived from a comparison of the absorption of picric acid and its ether dissolved in this solvent.

The theory that we have advanced, however, offers a completely satisfactory explanation of all the absorption results given by Buttle and Hewitt. The absorption of both mono- and di-nitrophenols is due to the play of forces between the residual affinities of the phenol residue and the nitro-groups. The position of the absorption band depends on the absorption of the phenol residue and the number and position of the nitro-groups. When the absorption of the phenol group is shifted nearer to the red by conversion into the sodium salt, so is the spectrum of the substituted phenol also shifted in the same manner. In trinitroanisole it is evident that the single hydroxyl group is insufficient to counteract the restraining influence of the three nitro-groups. When, however, the influence of the hydroxyl is enhanced by conversion into the sodium salt, then it is sufficiently powerful to overcome the restraint of the nitro-groups, but the absorption produced is not so near the red as in the dinitrophenoxides.

It is interesting to note that with the exception of trinitroanisole, the abnormality of which is noted above, all the nitro-compounds containing the hydroxyl or amino-groups in the ortho-position with respect to the nitro-group give evidence of two bands, whilst the para-isomerides only show one absorption band. The reason for this is not clear, but it seems to be characteristic of nearly all ortho-disubstituted benzenes with two powerful groups of different type. We propose to investigate this more fully in the hopes of determining the origin.

There remains now to be described the very remarkable influence that the nature of the solvent has on the absorption of the substituted nitro-compounds. Although no definite relation has as

yet been found, all our results show that an increase in the residual affinity of the solvent causes a shift in the absorption bands towards the red. It has been known for some time that, whilst nitroquinol dimethyl ether in the solid state and in alcoholic solution is strongly yellow, the solution of this compound in light petroleum is quite colourless. We have also noticed that the same is true for α -nitronaphthalene and 4-nitro-*o*-xylene. Also we find that aqueous solutions of these compounds are even more strongly coloured than the alcoholic solutions. We have examined the absorption spectra of many of these compounds in different solvents, and find that the colour changes are simply due to shifts in the positions of the absorption bands. The solvents used were light petroleum, alcohol, water, chloroform, benzene, pyridine, and aniline. In the case of the light petroleum, Kahlbaum's best material was used (b. p. $30-50^{\circ}$, for the determination of fat), and it was shaken for many hours with concentrated sulphuric acid in order to remove small quantities of some unsaturated substances present, which produce a marked absorption. After this treatment the material has very slight absorption in short layers. The three last solvents have, of course, very considerable absorption, and could only be used in those cases where the absorption band of the nitro-compound is sufficiently far from the ultra-violet.

Nitroquinol dimethyl ether was examined in all the above solvents, and the position of the absorption band, as can be seen from the curves in Fig. 8, varies considerably. The position of the head of the absorption band in the various solvents is shown in the following table:

	$1/\lambda$.
Light petroleum	3000
Benzene	2900
Alcohol	2800
Chloroform	2750
Pyridine	2730
Water }	2680
Aniline }	

A maximum variation of 320 units is thus shown in the case of this substance.

Again, 4-nitro-*o*-xylene exhibits in alcohol an absorption band with head at $1/\lambda=3550$, whilst in petroleum solution the head lies at $1/\lambda=3720$ (Fig. 3).

With α -nitronaphthalene, the position of the band is as follows (Fig. 2):

	$1/\lambda$.
Light petroleum	3200
Alcohol	3100
Benzene	3050

In β -nitronaphthalene, all three bands are nearer the red in

alcoholic solution, and they are in fact, in petroleum solution, as can be seen in Fig. 2.

An analogous observation was made in the case of the three nitrotoluenes, for here it was found that a difference in the absorption occurs with the strength of the solution. As can be seen from Fig. 1 (full curves), the absorption band is most pronounced when $N/1000$ solutions are examined. If equivalent lengths of $N/10,000$ solutions are observed, the absorption band is less persistent (Fig. 1, dotted curves).

We would point out as a result of the observations in different solvents of the substituted nitro-compounds in which no quinonoid structure is possible, that strong presumptive evidence is obtained against the quinonoid configuration of the nitrophenols. For whereas the increase in the residual affinity of the solvent can produce a shift in the absorption bands by so great an amount where no change in configuration occurs, it is not unreasonable to argue against a radical change in configuration when an increase in the residual affinity of one of the substituent groups (OH to ONa) produces an exactly similar change, although perhaps sometimes rather greater in amount. We feel therefore that the chain of evidence against there being any radical difference between the structure of the nitrophenols and their sodium salts is completed by these observations, and therefore are bound to express ourselves against the quinonoid configuration of the nitroanilines and the sodium nitrophenoxides.

In conclusion, we wish to express our cordial thanks to Professor Crossley for his courtesy in supplying us with the nitro-derivative of *o*-xylene, and also to the Research Fund Committee of the Chemical Society for a grant in aid of this investigation.

UNIVERSITY OF LONDON, UNIVERSITY COLLEGE, •
SPECTROSCOPIC LABORATORY.

LX.—The Isolation of Stable Salt Hydrates, with Special Reference to the Stable Hydrates of Sodium Carbonate.

By ALEXANDER CHARLES CUMMING.

THE actual existence of a number of salt hydrates which have been described must be regarded at present as an open question. Twelve hydrates of sodium carbonate have been described, yet Ketner (*Zeitsch.*

physikal. Chem., 1902, 39, 645) is only able to form three, whilst Müller-Erbach (*Ber.*, 1884, 17, 1417) had decided that there were but two hydrates. This instance illustrates the need for further criteria of the existence of hydrates, since, according to the descriptions, all twelve hydrates might have been stable hydrates. New hydrates are usually isolated incidentally in the course of solubility determinations or research of a similar nature. In general, the main purpose of the experiment is not the isolation of a new or of any particular hydrate, and a brief review of these methods will show that they are not for the most part well adapted to their secondary purpose, namely, the isolation of hydrates.

Solubility Method.—The solubility curve of a substance which forms hydrates may show a break at a transition temperature. Crystallisation above this temperature will yield a lower hydrate, or the anhydrous salt, whilst crystallisation below this temperature will yield a higher hydrate. The break in the solubility curve may, however, not be obtained, as the transition temperature may be outside the range of convenient or possible measurement; thus the solubility curve for copper sulphate (Landolt-Börnstein, *Physikalisch-chemische Tabellen*, 1905, p. 537) offers no evidence of the existence of any hydrate other than the pentahydrate. Further, the solubility of a hydrate may in many cases be measured in a region where it is unstable, and this might easily lead to the non-detection of another hydrate.

The existence of a hydrate may be detected by observation of a transition point from the solubility curve or by other methods, such as the dilatometer method, but it may still remain a matter of great difficulty to isolate the indicated hydrate.

Calorimetric Method.—The existence of a hydrate may be detected from measurements of the heats of solution of the salts in various states of hydration (Thomsen, *Thermochemistry*, English translation, 1908; Donnan and Hope, *Trans. Faraday Soc.*, 1909, 5, 244). The method is troublesome, and may not yield definite results, as, for example, Donnan and Hope have shown that this method does not reveal the existence of copper sulphate trihydrate, although it proves definitely that copper sulphate forms a monohydrate.

Vapour Pressure Method.—Another method which is not open to these objections is the measurement of vapour pressures of mixtures containing varied amounts of water. Lescœur (*Ann. Chim. Phys.*, 1890, [vi], 21, 511) was able to show in this way that there are only three hydrates of copper sulphate. This method is satisfactory if sufficient experiments are performed, but it is very laborious.

Desiccation with Sulphuric Acid.—If a mixture of a salt with an excess of water is placed over sulphuric acid in a closed vessel, it will be desiccated until a definite hydrate is left, provided that the aqueous

tension of the hydrate and employed it below that of the hydrate and greater than that of the next lower hydrate. If sufficient experiments are performed with various concentrations of sulphuric acid, it is possible to isolate all the stable hydrates of a salt. This is a practical method, and has found application in work by Ketner (*loc. cit.*) and others. Ketner states in a footnote that this method has long been used in the laboratory in Leyden.

Method under Investigation.—The method which has been investigated in this research is based on the same principle as that used in Leyden, but instead of desiccating with sulphuric acid, each hydrate was prepared by desiccation with the next lower hydrate, except in the case of the lowest hydrate, where the anhydrous salt was used as the desiccating agent.

It was shown by Andreae (*Zeitsch. physikal. Chem.*, 1897, 7, 241) that if three hydrates are placed in a closed vessel, the highest will lose water to the lowest until there are only two hydrates in the system. It may be pointed out that this is an interesting illustration of the Phase Rule. In one experiment Andreae placed a mixture of strontium chloride hexahydrate and dihydrate in one flask, a mixture of the dihydrate and anhydrous salt in another, and connected the two flasks. The first mixture lost water to the second mixture until all the hexahydrate had been converted into dihydrate, after which no further dehydration occurred. This obviously is a method for the preparation of strontium chloride dihydrate. Walker and Beveridge (*Trans.*, 1907, 91, 1797) have used this device for the preparation of *p*-toluidine monohydrate, and drew attention to the fact that a hydrate can be completely dried, without being decomposed, by the dehydrating action of the next lower hydrate, the lowest hydrate being prepared by the dehydrating action of the anhydrous substance. This should provide a method for the isolation of all the hydrates of any substance which are stable at the temperature of experiment. If a small supply of moist salt is exposed to the dehydrating action of the anhydrous salt, it should be dehydrated until the lowest hydrate is left. The total quantity of water to be taken up by the anhydrous salt must be less than sufficient to convert all of it into the lowest hydrate, so that a relatively large amount should be used. When the lowest hydrate has been isolated, it may be used to prepare the next in the series, and by continuation of the process the whole series of hydrates might be isolated. The process might also be carried out in the reverse direction, that is, the hydrates might be prepared by hydration, using the next highest hydrate in each case as the hydrating agent. Only stable hydrates have been referred to, since this method is unlikely to yield any information about hydrates unstable at the temperature of observation. Attention may be drawn also to the fact that the method

would fail if the temperature were raised above the transition temperature, since it is not possible to have three hydrates in equilibrium. Up to the present the only experimental data on the subject are contained in the researches of Andreas and of Walker and Beveridge. A further examination, therefore, appeared desirable, as the results would be interesting from the point of view of the Phase Rule. In the course of the research some information was obtained as to the rate of hydration and dehydration of hydrates under various conditions, a subject about which very little is known at present.

Hydrates of Sodium Carbonate.

It was decided to apply the method to the hydrates of sodium carbonate. An exact knowledge of the hydrates of such a common substance is obviously desirable, but very conflicting statements are to be found in the literature. Two hydrates are well known articles of commerce, namely, the monohydrate and the decahydrate. Hydrates have also been described with $1\frac{1}{2}$, 2, $2\frac{1}{2}$, 3, 4, 5, 6, 7, 8, and 9 molecules of water per molecule of sodium carbonate. Another hydrate, $\text{Na}_2\text{CO}_3 \cdot 15\text{H}_2\text{O}$, has also been described, but as it was prepared only at a low temperature it may be excluded from the present discussion. All of the above hydrates from the methods of preparation and properties given by the respective authors should be stable at the ordinary temperature, but Müller-Erbach (*loc. cit.*) could only isolate the monohydrate and decahydrate. Ketner (*loc. cit.*), by drying with various concentrations of sulphuric acid, obtained hydrates with 1, 7, and 10 molecules of water. Wells and Macadam, jun. (*J. Amer. Chem. Soc.*, 1907, 29, 721), in the course of careful solubility determinations, and Donnan and Hope (*loc. cit.*), from calorimetric analysis, found the same three hydrates as Ketner. These recent researches leave little doubt that there are only three stable hydrates of sodium carbonate, but in view of the earlier results, further confirmation appeared desirable, especially as none of the researches provides a rigid proof of the number of stable hydrates.

EXPERIMENTAL.

Preparation of Lowest Hydrate.—The preparation of the lowest hydrate may be described in some detail, as the experiment was typical of the method adopted.

On the floor of a vacuum desiccator were placed about 100 grams of anhydrous sodium carbonate. A small weighed quantity of the decahydrate, spread in a thin layer on a watch-glass, was then introduced, and the desiccator evacuated. The apparatus was kept in

a certain amount of water was lost. At the same time the substance on the watch-glass was found to have increased in weight. It was found that the weight of the substance on the watch-glass represented the lowest hydrate that is, the hydrate with the same vapour pressure as the mixture below, which was made up of originally anhydrous sodium carbonate plus the small amount of water obtained by dehydration of the decahydrate.

TABLE I.

Time in days.	Weight in grams.	Loss in grams.	Molecules H ₂ O per Na ₂ CO ₃ .
0	2.129	—	10.0
3	0.925	1.204	1.0
10	0.925	1.204	1.0
12	0.925	1.204	1.0

The substance lost water until Na₂CO₃.H₂O was left, after which no further dehydration was detected. In all the later experiments the substance was roughly ground at the start of an experiment. When the weight had become constant, it was ground to a fine powder, and the experiment continued. In no case was a further change in weight noticed with hydrates of sodium carbonate. The composition was calculated from the weight of water lost, and, as a check, the hydrate obtained was analysed, except in the first experiment, where this was not done.

Hydrate next above the Monohydrate.—An intimate mixture of anhydrous and decahydrated sodium carbonate was made in the proportion calculated to give the monohydrate, and the mixture was kept in an evacuated vessel for three weeks before use. A small weighed quantity of sodium carbonate was then dehydrated by a large amount of this mixture.

TABLE II.

Time in days.	Weight in grams.	Loss in grams.	Molecules H ₂ O per Na ₂ CO ₃ .
0	2.391	—	10.0
1	2.206	0.185	8.3
2	2.079	0.312	7.9
7	1.942	0.449	7.02
13	1.941	0.450	7.01
16	1.941	0.450	7.01

In this experiment the dehydrating agent was a mixture of anhydrous and decahydrated sodium carbonates in the proportion calculated to yield the monohydrate. As there was a real possibility that the monohydrate had not been formed, it was prepared in another way. The crystalline decahydrate was melted on a steam-bath and evaporated until a sufficient quantity of the monohydrate had separated. This was filtered from the hot solution. Analysis showed these crystals to have the empirical composition Na₂CO₃.1.2H₂O, that is, they were crystals of the monohydrate mixed

with a small proportion of a higher hydrate. A weighed sample of the decahydrate was then dehydrated by 100 grams of this monohydrate.

TABLE III.

Time in days.	Weight in grams.	Loss in grams.	Molecules H ₂ O per Na ₂ CO ₃ .
0	2.438	—	10.0
5	2.168	0.280	8.0
11	1.981	0.457	7.2
14	1.976	0.462	7.0
21	1.976	0.462	7.0

The substance was then finely ground. No further loss was detected after seventy-three days in an evacuated vessel.

Hydrate next above the Heptahydrate.—It was found that no dehydration of the decahydrate had taken place after seven days in an evacuated vessel above a mixture of hydrates which had the empirical composition $\text{Na}_2\text{CO}_3 \cdot 7.3\text{H}_2\text{O}$. There is no evidence, therefore, of any hydrate intermediate between the heptahydrate and decahydrate.

Hydration of a less Hydrated Salt.

In the previous experiments a hydrate was dehydrated by a lower hydrate until the hydrate next in the series to the lower hydrate was obtained. The process may be carried out in the reverse manner, that is, a substance may be hydrated by a higher hydrate until the hydrate next below the higher hydrate is formed.

Hydrate next below the Decahydrate.—A small weighed sample of the anhydrous salt was hydrated by a large supply of slightly effloresced decahydrate.

TABLE IV.

Time in days.	Weight in grams.	Increase in grams.	Molecules H ₂ O per Na ₂ CO ₃ .
—	1.717	—	—
1	2.123	0.406	1.4
4	2.328	0.611	2.1
11	2.673	0.956	3.3
15	2.777	1.060	3.6
19	2.900	1.183	4.1
25	3.238	1.521	5.2
28	3.805	1.588	5.5
39	3.540	1.823	6.3
50	3.722	2.005	6.9
96	3.788	2.021	6.93
216	3.788	2.021	6.93

The amount of water given in the last column is calculated from the gain in weight, on the assumption that the sample was quite anhydrous at the beginning of the experiment, but a trace of water must have been present, as analysis showed that the substance finally obtained was pure $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$.

It will be seen that the first molecule of water was taken up very quickly and the remainder at a much slower rate. This experiment taken alone indicates the probable existence of a monohydrate.

The existence of $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ was indicated in a similar manner during the dehydration of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ by anhydrous magnesium sulphate. One-seventh of the water was lost in the first day, and the dehydration then became extremely slow.

Hydrate next below the Heptahydrate.—A small weighed sample of anhydrous salt was hydrated with 100 grams of the heptahydrate.

TABLE V.

Time in days.	Weight in grams.	Increase in grams.	Molecules H_2O per Na_2CO_3
0	0.607	—	—
2	0.603	0.073	0.76
22	0.709	0.102	0.99
36	0.712	0.105	1.02
58	0.712	0.105	1.02

Highest Hydrate of Sodium Carbonate.—A small weighed quantity of anhydrous sodium carbonate was exposed to the hydrating action of a saturated solution with which was mixed a large supply of crystals.

TABLE VI.

Time in days.	Weight in grams.	Increase in grams.	Molecules H_2O per Na_2CO_3
—	0.735	—	—
1	1.210	0.585	4.7
2	1.379	0.644	5.2
3	1.566	0.831	6.7
4	1.633	0.896	7.2
7	1.753	1.018	8.1
11	1.853	1.118	9.0
37	1.985	1.250	10.01
51	1.985	1.250	10.01

The results in these tables have been expressed graphically in the diagram. The experiments were carried out at room temperature, and the mean temperature would be about 12° .

It is evident that with these hydrates, dehydration of a small quantity of substance provides a quicker process for the preparation of a hydrate than does the hydration method.

The two curves showing dehydration to the heptahydrate illustrate the difference in time produced by a slight variation in the conditions of the experiment. A first inspection of these results would suggest that a rigid proof has been obtained that there are three, and not more than three, stable hydrates of sodium carbonate. The existence of the three hydrates with 1, 7, and 10 molecules of water is certainly proved, but consideration will show that the existence of

with the glass. Some of the drops were formed on a platinum wire which had been placed on the surface of a crystal of sodium carbonate decahydrate. Each drop as it was touched crystallised instantly and completely, which proved that a supersaturated solution had been formed instead of the expected solid decahydrate phase. In the course of the first few days all the drops crystallised, with the exception of two minute drops. These were still present at the end of thirty-seven days, and when these were touched they did not crystallise completely. The formation of the drops of supersaturated solution at the beginning of the experiment is mainly remarkable in that there cannot have been any nucleus present to start the formation of decahydrate, despite the fact that the floor of the vessel was covered with moist crystals of the decahydrate. The supersaturated solution would have a lower vapour pressure than the wet decahydrate system and would therefore continue to absorb water. In absence of a nucleus of decahydrate, the absorption of water would continue, if it is to be supposed, until these drops had the same vapour pressure as the system below, that is, until a "saturated solution" had been formed. This agrees with the fact that only partial crystallisation occurred when the drops were artificially seeded, since the liquid left after the crystallisation must have been "saturated solution." If this explanation be accepted, "saturated solution" was formed without formation of the intermediate phase, the decahydrate. The experiment has been repeated three times, and in two cases the solution phase was formed. In all cases most of the salt hydrated directly to the solid hydrate, but small detached drops of solution formed in places on the glass.

Method for the Isolation of a new Hydrate.—From the results obtained with sodium carbonate it might seem that the method outlined in the earlier part of this paper would quickly lead to the isolation of all the hydrates of any salt. From experiments with other salts, however, it appears that sodium carbonate is a particularly favourable case, and a considerable search may be necessary before another salt is found which yields a series of hydrates so quickly and completely at the ordinary temperature. Magnesium sulphate heptahydrate, dehydrated by anhydrous magnesium sulphate, lost one seventh of its water in the first twenty-four hours, and then lost water steadily but very slowly. At the end of one hundred and forty-five days the additional amount of water lost corresponded with a loss of only half a molecule of water, and there was no appreciable increase in the rate of dehydration after fine grinding. With several other salts it was found that hydration or dehydration may occur with extreme slowness. From the experience gained in this research, I am of opinion that the systematic search for all the hydrates of a salt

would in most cases prove more tedious and costly than to repay the labour. At the same time it appears probable that the existence or otherwise of any particular hydrate may be readily determined by means of this method. The method has the further important practical advantage that if the hydrate has any existence it will be obtained in a pure state. If the existence of a hydrate with n molecules of water is suspected, two experiments should be performed.

On the floor of a desiccator place a quantity of an artificial finely powdered mixture which contains a little less than n molecules of water per molecule of anhydrous salt. On a watch-glass above it place a little finely powdered mixture, with a little more than n molecules of water, and exhaust the vessel. The substance on the glass will lose water until the pure hydrate is left, if there is a stable hydrate of that composition. This was the method used by Walker and Beveridge for the preparation of *p*-toluidine monohydrate. I would suggest that a second experiment should be performed, using a large quantity of a mixture containing slightly more than n molecules of water to hydrate a small quantity of a mixture with slightly less than n molecules of water. In all cases it is expedient to evacuate as thoroughly as possible. The method would probably be of value in organic chemistry for the preparation in a pure state of substances which readily dissociate into their constituents, such as iodine additive compounds and alcohol additive compounds corresponding with hydrates (alcoholates).

Suspended Transformation.—A curious case of suspended transformation was noticed in some experiments with the hydrates of copper sulphate. The dehydrating agent was a large supply of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ in the form of a fine powder mixed with a small proportion of powdered pentahydrate. A small weighed quantity of the pentahydrate was to be dehydrated. The pentahydrate had been recrystallised, and was ground to a coarse powder before a sample was taken. It was found that 2.282 grams had lost in two days only 0.004 gram of water, and the colour of the crystals was unchanged. After three more days the weight was unchanged. The crystals were then touched with a platinum spatula, which had been dipped in the mixture below. No weighable quantity had been added, but a nucleus of a lower hydrate had evidently been introduced, as efflorescence started in two places and spread through the whole mass.

Time in days	Weight in grams.	Loss in grams.	Molecules H ₂ O per CuSO ₄
0	2.282	—	5.0
2	2.278	0.004	—
5	2.278	0.004	—
12	1.928	0.354	3.69
33	1.914	0.368	3.62
145	1.847	0.435	3.37
175	1.839	0.443	3.35
182	1.830	0.452	3.31
212	1.795	0.487	3.18

From this table it will be seen that once the action had started, dehydration proceeded steadily, but so slowly that it had not attained completion in seven months. The suspended transformation in this experiment is interesting, in that the vapour pressure in the apparatus was fixed by the presence of a mixture of monohydrate with a little trihydrate on the floor of the vessel. The initial small loss probably indicates a trace of surface moisture, and it is possible that on this account the grinding did not start the formation of a lower hydrate.

CHEMISTRY DEPARTMENT,
UNIVERSITY OF EDINBURGH.

LXI.—*Affinity Relations of Cupric Oxide and of Cupric Hydroxide.*

By ARTHUR JOHN ALLMAND.

In the course of a recent paper (Trans., 1909, 95, 2151), the author showed that crystalline cupric hydroxide when treated with concentrated alkali solutions at the ordinary temperature, or when shaken with dilute aqueous ammonia at 25°, loses its water and is converted into cupric oxide. According to these facts, crystalline cupric hydroxide is unstable with respect to cupric oxide and the given aqueous solution at the temperatures in question, whereas the reverse has been thought to be the case. To decide this point tensimetric and electrometric experiments were undertaken. If in reality crystalline cupric hydroxide constitutes an unstable system at the ordinary temperature, it must have a higher vapour pressure than water, or the alkaline and ammoniacal solutions referred to, and yet it appears to be perfectly stable in dry air. Secondly, it must also be more soluble than cupric oxide, and the system $\text{Pt} \begin{vmatrix} \text{CuO} \\ \text{Cu}_2\text{O} \end{vmatrix} \text{alkali}$ should give

a lower single bond.

alkali, although it is not certain a precipitate will be sufficiently great to be detected.

Tensimetric Experiments.

A tensimeter was filled with all the ordinary precautions. One limb contained a sample of "Becquerel" cupric hydroxide (*Compt. rend.* 1862, 34, 573), which had been dried at 100°, bottled, and subsequently left in a desiccator over calcium chloride. The other limb contained phosphoric oxide, and the indicating liquid in the U-tube was olive oil. The tensimeter was placed in a thermostat at 25°. Readings were taken over some four months, at the end of which time the cupric hydroxide had undergone no marked change in colour. The following table contains the results.

TABLE I. Temperature 25°.

Time of observation.	Reading in mm. of olive oil.
September 27	Filled and sealed: kept limbs in connexion.
" 28	Allowed oil to flow into U-tube; placed in thermostat.
" 29	7
" 30	8
October 2	9—10
" 4	9—10
" 6	9—10
" 20	13—14
November 2	13—14. Took out, and allowed limbs to stand in connexion 15 hours. Replaced. Reading rises very slowly.
" 15	3—4
" 29	3—4. Put limbs once more in connexion for 15 hours. Replaced.
December 1	3—4
" 7	2—3
" 9	2—3
" 11	2
" 15	<2
" 21	<2
January 6	1.5. Put limbs into connexion once more for 24 hours. Replaced.
" 20	1.5

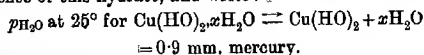
The vapour pressure of water at 25° is about 23.5 mm. of mercury, whilst the highest pressure observed in the tensimeter was about 13.5 mm. of olive oil. This supported the view that cupric hydroxide is the stable system. It was, however, possible that the dehydration did not commence, owing to powerful opposing reaction resistances, and that by the addition of some quantity of a decomposition product the reaction resistances could be overcome. A second tensimeter was therefore filled, containing in one limb a mixture of cupric

by the action of
measurements
the following table:

TABLE II. Temperature 25°.

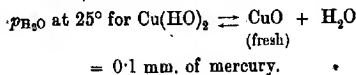
Time of observation.	Reading in mm. of olive oil.
September 2	Started
" 7	9
" 9	9.5
" 11	11.5
" 15	11.5
" 21	12.5
January 5	13.5. Placed limbs in connexion for 24 hours.
" 20	1.5 Replaced.

It will be seen that the figures are practically identical with those in table I, furnishing further evidence in favour of the view that crystalline cupric hydroxide is stable with respect to copper oxide and water. The fact that the same two final figures—13.5 mm. and 1.5 mm.—occur in both tables points to their corresponding with two definite equilibrium states. It has been already shown (*loc. cit.*) that crystalline cupric hydroxide contains more water (in the ratio 1.07:1) than is demanded by the formula $\text{Cu}(\text{HO})_2$, and that it is improbable that this excess is physically held or adsorbed. It was suggested that the excess may be due to the presence of small quantities of higher hydrate, such as $\text{CuO} \cdot 2\text{H}_2\text{O}$. If that view be taken, we can perhaps ascribe the higher of the two vapour pressures observed to the presence of this hydrate, and write:



(The specific gravity of olive oil is taken as 0.9.)

In any case it is highly probable that the lower vapour pressure measured corresponds with the dehydration of cupric hydroxide to copper oxide and water, and we can write:



Electrometric Measurements.

The electrode measured was always of the type $\text{Pt} \left| \begin{array}{l} \text{CuO} \\ \text{Cu}_2\text{O} \end{array} \right. \text{alkali}$. With the exception of a few experiments carried out with *N*-potassium hydroxide and *N*/10-sodium hydroxide, the electrolyte employed was *N*-sodium hydroxide (carbonate-free). The electrode vessels were adapted for shaking and similar to those already described (*loc. cit.*), whilst the measuring apparatus—galvanometer, Weston element,

metre bridge—calls for no special treatment. The electrodes were gently revolved on a wheel, shaken, and taken on and measured against calomel electrodes at various intervals for some length of time. All readings were made at the ordinary temperature, namely, 17° . The potential of the *N*-calomel electrode was taken as $+0.282$ volt at 17° ; the liquid potential difference between *N*-potassium chloride and *N*-sodium hydroxide as 0.020 volt.

In the first experiments, cupric oxide was used, prepared by thorough ignition of cupric hydroxide or cuprous oxide over a Bunsen burner. Now the single potential difference given by the system $\text{Pt} \mid \text{Cu}(\text{HO})_2, \text{N-NaOH}$ is -0.074 volt (*loc. cit.*), and judging from the results of the vapour-pressure measurements, the combination $\text{Pt} \mid \text{CuO}, \text{N-NaOH}$ should give a more positive value, corresponding with a tendency for the change $\text{CuO} + \text{H}_2\text{O} \rightarrow \text{Cu}(\text{HO})_2$ to take place. As a matter of fact, the behaviour of the electrodes was as follows. They commenced (read the day after setting up) by giving considerably more negative values than the cupric hydroxide electrode, and then slowly fell, becoming more and more negative, and in some cases finally reaching or approaching an asymptotic value. For example, an electrode set up containing *N*-sodium hydroxide and cupric oxide, prepared by igniting cuprous oxide, gave the following readings.

TABLE III. Temperature 17° .

Days after setting up.	Single potential $\text{Pt} \mid \begin{smallmatrix} \text{CuO} \\ \text{Cu}_2\text{O} \end{smallmatrix} \text{N-NaOH}$.
1	-0.096 volt
3	-0.109 "
4	-0.112 "
5	-0.114 to -0.115 volt
6	-0.117 "
7	-0.118 "
8	-0.119 "
10	-0.120 "
11	-0.120 to -0.119 "
12	-0.120 to -0.119 "
14	-0.121 to -0.122 "

The rate of fall of potential was very different in different cases, as was also its extent. The first explanation which suggests itself is that the electrode is not acting reversibly. Of electrode systems in which the reaction taking place is not the complete discharge of an ion to a neutral substance, but only an increase or decrease in the number of ionic charges, it is known that but few behave reversibly, and this is particularly the case in alkaline solutions. On the other hand, the particular reaction $\text{Cu}^{++} \rightleftharpoons \text{Cu}^+ + \oplus$ is reversible in acid solution,

and the behaviour of the Pt $\left| \begin{smallmatrix} \text{Cu}(\text{HO})_2 \\ \text{Cu}_2\text{O} \end{smallmatrix} \right.$ alkali electrode to assume that it is also reversible in alkaline solution. Luther (*Zeitsch. Elektrochem.*, 1907, 13, 289) has declared the criteria of irreversibility of an electrode to be (amongst others): (1) fluctuations in potential value; (2) two electrodes in the same solution giving different values; (3) changes on shaking, and (4) changes in concentration of the electrolyte not bringing about the corresponding theoretical potential changes.

In the present case, the variation in potential was always a directed one—a fall. To test the second point an electrode vessel was made up containing two electrodes (one blank and one platinised) about 2 cm. apart, dipping into the same mixture of depolariser and electrolyte. They were measured over a period of five weeks, during which time the potential fell by 0.025 volt, and they always agreed to within 0.0004 volt. It was further found that shaking never altered the potential of any electrode by more than a millivolt, and the original value was restored within a minute or two on standing.

Pt $\left| \begin{smallmatrix} \text{Cu}(\text{HO})_2 \\ \text{Cu}_2\text{O} \end{smallmatrix} \right.$ alkali electrodes gave the theoretical change on altering the concentration of the alkali (slight deviations could be otherwise explained), and a few experiments carried out with Pt $\left| \begin{smallmatrix} \text{CuO} \\ \text{Cu}_2\text{O} \end{smallmatrix} \right.$ alkali electrodes, using alkali of different concentrations, gave indication of the same behaviour. That cupric hydroxide is really far more soluble than cupric oxide is also shown by the fact that, whereas the former when shaken up with alkali and an excess of finely-divided copper is completely converted into cuprous oxide within a few days, cupric oxide was found to be only altered slightly by a month's shaking. It seems justifiable to assume therefore that the electrode is acting reversibly, and giving the true potential corresponding with the relative concentrations in the solution at any moment of Cu^{++} and Cu^+ ions.

This being so, the only other explanation open is that some kind of change is taking place in the copper oxide, rendering it less soluble. This view seems particularly plausible, as cupric oxide is not crystalline but amorphous, and as such is subject to the phenomenon of *aging*, which is bound up with a progressive decrease in solubility. The nature of this process is still obscure. It has been regarded as the result of a slow crystallisation taking place in the amorphous mass, looking on the latter as a supercooled liquid. This does not seem very probable, as the solubility of the material should not then appreciably alter until completely changed into crystalline substance. The phenomenon is particularly well marked in the cases of precipitated colloidal substances (*Zeitsch. anorg. Chem.*, 1899, 20, 185; 1900, 25,

155; 1901, 27, 390; 1901, 28, 473; 1902, 30, 311; 1904, 38, 377; 1904, 40, 428; 1905, 46, 333, etc.). It is there accompanied by a probable loss of water, and by a striking decrease in the bulk and surface of the precipitate, and Hantzsch (*Zeitsch. anorg. Chem.*, 1902, 30, 338) has ascribed the lowering in solubility to both chemical and physical reasons, the former depending on the supposed molecular dehydration which accompanies the ageing, and the latter being due to the great decrease in surface which is the result of the spontaneous coagulation of the material. Ostwald (*Zeitsch. physikal. Chem.*, 1900, 34, 395) had previously advanced the conception of dependence of solubility on surface or size of grain to account for the differences displayed between the red and yellow forms of mercuric oxide, and the idea was further extended to other substances (all crystalline) by Hulett (*Zeitsch. physikal. Chem.*, 1901, 37, 385), Hulett and Allen (*J. Amer. Chem. Soc.*, 1902, 24, 667), and von Steinwehr (*Zeitsch. Elektrochem.*, 1906, 12, 578). It has been lately shown (Trans., 1909, 95, 2151, and unpublished work of the author) that the initial decrease observed in the single potential readings of the system $\text{Pt} \left| \begin{array}{c} \text{Cu}(\text{HO})_2 \\ \text{Cu}_2\text{O} \end{array} \right| \text{alkali}$ and $\text{Hg} \left| \text{HgO} \right| \text{alkali}$ can be ascribed to a spontaneous diminution in solubility due to the same cause.

In the present case the author is disinclined to adopt that explanation. As will be seen, the difference between the highest and lowest values experimentally obtained with the $\text{Pt} \left| \begin{array}{c} \text{CuO} \\ \text{Cu}_2\text{O} \end{array} \right| \text{alkali}$ electrodes is 0.093 volt, which corresponds with a ratio of solubilities in the two cases of about 40:1. On the other hand, the greatest ratio in which the solubility of a substance has been increased by alteration of the surface conditions is 3:1 (Hulett, *loc. cit.*). Further, the colloidal hydroxides to which Hantzsch has applied Ostwald's conception do certainly show a very remarkable diminution of surface when ageing, whilst the samples of copper oxide with which the author has worked undergo no such change.

A more probable explanation is that the phenomenon is due to gradual polymerisation of the molecules of the copper oxide, and that at any moment between the time of preparation of the fresh substance and the time of complete ageing we have a solid solution containing two (or more) kinds of molecules of different complexity in proportions which do not correspond with the equilibrium ratios. Assuming, then, that the more complex molecule is the less soluble, and that the freshly prepared material has an undue preponderance of simple molecules, the solubility of a sample of copper oxide will slowly fall, until a value has been reached corresponding with the equilibrium concentrations of the different kinds of molecules. When shaken up with something

which can alter solvent action, the velocity of the process will be increased. Alkali solutions must have that effect, owing to the slight amphoteric nature of the copper oxide; and it is found by experience that left to itself, the oxide alters very slowly indeed, but that it ages in contact with alkali, and more rapidly in a concentrated than in a dilute alkaline solution. We will adopt this polymerisation conception as a working hypothesis. Then it is very probable that the equilibrium of the different kinds of molecules will shift with increase of temperature, and in favour of the less associated molecule, the formation of which is probably accompanied by absorption of heat. Further, the rate at which equilibrium is reached will be greater the higher the temperature; and consequently, until equilibrium has set in, determinations of solubility, potential difference, dissociation pressure, etc. (all of them related quantities) will yield results depending to a greater or less extent on:

- (a) Temperature of preparation of sample.
- (b) Time during which it was kept at that temperature.
- (c) Rate of passage from temperature of preparation to temperature of measurement.

And the influence of the temperature of measurement will be a two-fold one, due to:

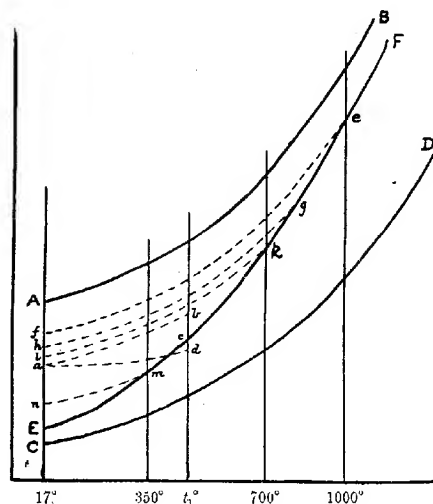
- (a) The change of solubility, etc., of each different kind of molecule with change of temperature, and
- (b) The variation in the relative proportions of the different kinds of molecules with change of temperature.

In Fig. 1, temperature is plotted along the abscissa and along the ordinate solubility or dissociation pressure of the oxide. AB would represent the curve supposing all the molecules to be simple, and CD supposing them all to be complex, whilst EF is the actual equilibrium curve, which moves nearer to AB as the temperature rises, corresponding with a decrease in the proportion of the more complex molecules.

With the simple assumptions already made, it is possible to trace qualitatively on the above curve the behaviour of any sample of copper oxide on heating or cooling or measurement. Let, for example, the line AEC correspond with 17° , at which temperature a specimen of copper oxide is made by withdrawing water from cupric hydroxide. It will initially have the dissociation pressure corresponding with A . This will fall pretty rapidly at first along the line AE . Suppose when the point a is reached the oxide be heated to a temperature t_1° . If no further polymerisation were to take place, its path would be along the line ab . Polymerisation will continue, however, and the more rapidly the higher the temperature (although the closer proximity of the curves ab and Ec at the higher temperature will tend to diminish the rate of change). The actual path followed then will fall

below ab , but close to it if the temperature be raised rapidly. If the temperature be raised *very* slowly, then the equilibrium curve Ec will be reached proportionately sooner, and followed until c is reached. At intermediate or variable rates of increase of temperature, the line bc may finally be struck, or the curve Ec cut, and a point below it, such as d , ultimately reached. Hence, at the temperature t_1° the initial dissociation pressure given by the oxide may be equal to, greater than, or less than the equilibrium value.

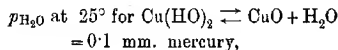
FIG. 1.



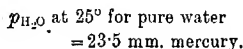
We will now attempt to interpret the single potential readings which were obtained for the system $\text{Pt} \left| \begin{array}{c} \text{CuO} \\ \text{Cu}_2\text{O} \end{array} \right| \text{N-NaOH}$ in terms of the conception developed above.

1. *Value of Point A* (Fig. 1).—This is not given directly by electrometric measurements, but can be deduced from the tensimeter readings already discussed.

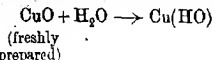
We have:



and



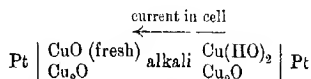
Hence the decrease in free energy of the reaction



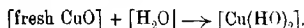
$$\begin{aligned} \text{at } 25^\circ \text{ is } RT \ln \frac{23.5}{0.1} \\ = 0.06 \log. 235 \text{ volt-faradays} \\ = 0.06 \times 2.37 \text{ volt-faradays.} \end{aligned}$$

It will not be very different at 17° .

If the cell



were to be set up, the chemical result for the passage of *one* faraday would be the same reaction, namely:



$$\begin{aligned} \text{Hence } E.M.F. &= 0.06 \times 2.37 \text{ volts} \\ &= 0.142 \text{ volt.} \end{aligned}$$

$$\text{We know that Pt} \left| \begin{array}{c} \text{Cu}(\text{HO})_2 \\ \text{Cu}_2\text{O} \end{array} \right| N\text{-NaOH} = -0.074 \text{ volt}$$

Therefore,

$$\begin{aligned} \text{Pt} \left| \begin{array}{c} \text{fresh CuO} \\ \text{Cu}_2\text{O} \end{array} \right| N\text{-NaOH} \\ = +0.068 \text{ volt.} \end{aligned}$$

2. *Value of Point E* (Fig. 1).—For this value the author has taken the lowest figure reached in any of the measurements, that is, -0.154 volt. It was obtained with a sample of cupric oxide prepared by ignition of cupric nitrate. As the accompanying figure (2) shows, it was approached asymptotically, which fact supports the view that it represented the true equilibrium value. The other curve on the same diagram was given by a sample of oxide obtained by ignition of cuprous oxide. Although not followed to the end (the electrode vessel broke), it appears likely that it would have reached the same limiting value. As we shall see later, there is another reason for thinking that -0.154 volt is very near the correct value.

3. *Samples of Oxide aged at 950 – 1000°* .—Some cupric oxide (i), prepared by igniting crystalline cupric hydroxide, was placed in a platinum crucible and heated in a platinum-wound electric heater

at 800 – 900° for 3 hours.
 „ 900 – 950 „ 1 hour.
 „ 950 – 1000 „ 3 hours.
 „ 1000° „ 1 hour.

A second sample (ii), also from cupric hydroxide, was similarly heated

at 800–900° for 1½ hours.

„ 900–950 „ 2½ „

„ 950–970 „ 8 „

In both cases the oxide was allowed to cool in the furnace after shutting off the current. The following readings resulted, using electrodes containing the above oxides.

FIG. 2.

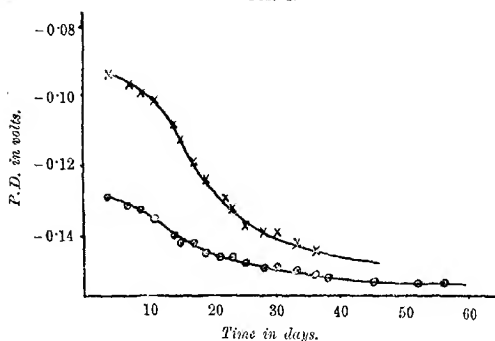


TABLE IV. Temperature 17°.

Time after setting up.	Potential Pt $\left\{ \begin{array}{l} \text{CuO} \\ \text{Cu}_2\text{O} \end{array} \right.$ N-NaOH in volts.	
	(i)	(ii)
1 day	-0.061 volt	—
2 days	—	-0.063 volt
5 „	-0.064 „	—
9 „	-0.067 „	—
13 „	—	-0.073 „
20 „	-0.076 „	—
22 „	—	-0.078 „
29 „	—	-0.081 „
36 „	—	-0.084 „

Referring to Fig. 1, it is seen that for a high temperature, such as 1000°, at which equilibrium will be quickly reached, and at which the proportion of simple molecules is comparatively high, the copper oxide dissociation pressure will correspond with a point such as *e*. If suddenly chilled, the ratio of the different molecular species would remain unaltered, and the falling dissociation pressure would follow the line *ef*. When measured electrometrically at room temperature, a very high initial value would result. If cooled more slowly, as was

actually the case, the curve *EF* would probably be followed for some time and then gradually left, the path *egh* being taken. The point, *h*, finally reached would correspond with the initial potential value, -0.061 volt, given by these oxide samples. It is interesting to notice that these samples of oxide when first measured were unstable with respect to cupric hydroxide, the potential $\text{Pt} \left| \begin{array}{c} \text{Cu}(\text{HO})_2 \\ \text{Cu}_2\text{O} \end{array} \right. N\text{-NaOH}$ being -0.073 volt.

4. *Samples of oxide prepared by ignition of cupric nitrate, cupric hydroxide, or cuprous oxide in an open porcelain crucible over a Bunsen flame.*—The results of some of the preparations are shown in table III and in Fig. 2. Other figures were as follows :

TABLE V. Temperature 17°.

Time in days after setting up.	Single Potential Pt $\left \begin{array}{c} \text{Cu}_2\text{O} \text{ N-NaOH} \\ \text{CuO} \end{array} \right.$ in volts.			
	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>
1	-0.103	-0.107	$\left. \begin{array}{l} -0.107 \\ -0.110 \end{array} \right\}$	-0.097
2	-0.118	$\left. \begin{array}{l} -0.109 \\ -0.112 \end{array} \right\}$	—	—
3	-0.123	-0.114	$\left. \begin{array}{l} -0.114 \\ -0.115 \end{array} \right\}$	—
4	-0.125	-0.115	—	—
14	—	—	—	-0.106
23	—	—	—	-0.113
30	—	—	—	-0.115
37	—	—	—	-0.118

These preparations were never subjected to such a high temperature as those discussed under (3), and they were also cooled far more rapidly. During this process one would expect them to follow nearly the line *kl*, falling a little below it only. The value *l* corresponds with the initial figure of -0.097 to -0.107 volt given in the table. The differences observed will be the result, amongst other things, of differences in time of heating, rate of cooling, etc.

5. *Samples of Oxide aged at 350°.*—Two samples of crystalline cupric hydroxide contained in porcelain crucibles were heated in a nickel-wound electric heater to 330–350° for twenty hours. The crucibles were then taken out and allowed to cool. Two electrodes were made up and measured in the ordinary way. They gave :

(a) -0.135 (2nd day); -0.134 (13th day).

(b) -0.133 (3rd day); -0.133 (10th day); -0.135 (17th day).

There was thus hardly any alteration during the time of measurement, and, moreover, the two sets of figures agree very well with one another. From this fact we conclude that equilibrium was probably reached in the two cases, and frozen by the rapid cooling,

during which the dissociation pressure would follow the line *mn*. Thus, a low initial value would result.

6. *Samples of Oxide prepared at low temperatures.*—Oxide was prepared by dehydrating cupric hydroxide with aqueous ammonia at 25° and with aqueous potassium hydroxide at 70°. The potential values of electrode systems containing preparations of oxides thus made only fell very slowly; although in one case measured for five weeks, values lower than -0.117 volt were never reached, as the table shows:

TABLE VI. Temperature 17°.

Time in days after setting up.	Potential difference Pt $\left \begin{smallmatrix} \text{CuO} \\ \text{Cu}_2\text{O} \end{smallmatrix} \right.$ <i>N</i> -NaOH in volts.						
	1.	2.	3.	4.	5.	6.	7.
1	—	-0.106 } -0.109 }	-0.108 } -0.109 }	—	-0.099 } -0.100 }	-0.011	-0.102
2	-0.106 } -0.109 }	-0.113 } -0.114 }	—	—	-0.100	—	—
3	-0.114	—	—	—	-0.102	—	—
4	-0.115	-0.116	—	-0.111	—	-0.113	-0.108
5	—	—	—	—	-0.105	-0.114	—
6	—	—	—	—	—	—	-0.111
7	—	—	—	-0.111	—	-0.113	—
8	—	—	—	—	-0.105	—	—
9	—	—	—	-0.113	—	-0.116	-0.111
10	—	—	—	—	-0.105	—	—
11	—	—	—	-0.114	—	-0.115	—
12	—	—	—	—	—	—	-0.114
13	—	—	—	—	-0.107	—	—
14	—	—	—	-0.114	—	—	-0.116
16	—	—	—	—	-0.107	—	—
18	—	—	—	—	-0.108	—	—
19	—	—	—	-0.113	—	—	—
25	—	—	—	—	-0.111	—	—
28	—	—	—	—	—	—	-0.116
32	—	—	—	—	-0.113	—	—
35	—	—	—	—	-0.112	—	—

It is evident that reference to Fig. 1 can interpret satisfactorily the initial values given by the different electrodes, but gives no explanation of the reason for the very different rates of ageing at 17° of samples of copper oxide which have been heated to different temperatures. It has been seen that oxide which has been heated to 1000° alters slowly and regularly, that oxides which have been prepared at temperatures of 700—800° age at varying speeds, and that oxides heated only to 350° or below alter very slowly indeed. It is probable that these differences are due to variations in the nature of the surface of the material or to similar causes, but more it is impossible to say. Apart from this point, if the view developed here that the changes observed during ageing are the result of polymerisation be accepted as correct, it is obvious that electromotive measurements may prove to be

a very valuable method for the investigation of the molecular complexity of certain solid substances.

It should be mentioned here that Immerwahr (*Zeitsch. Elektrochem.*, 1900-1, 7, 477), Johnson (*Trans. Amer. Electrochem. Soc.*, 1902, 1, 187), and Lorenz and Hauser (*Zeitsch. anorg. Chem.*, 1906, 51, 81) have all worked on electrodes of the type $\text{Cu} | \text{CuO}$ alkali, which, however, have been shown by the author to be unstable, owing to cuprous oxide formation. It is interesting to note that Immerwahr found that oxide prepared from copper nitrate gave much more negative values than oxide prepared by precipitation from hot aqueous solution by alkali.

Calculations of Affinity Values.

We are now in a position to understand the relationships to one another of cupric hydroxide and cupric oxide. We have the following three potential differences at 17° :

$$\text{Pt} \left| \begin{array}{l} \text{fresh CuO} \\ \text{Cu}_2\text{O} \end{array} \right. N\text{-NaOH} = +0.068 \text{ volt.}$$

(Calculated approximate
probable value)

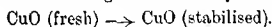
$$\text{Pt} \left| \begin{array}{l} \text{Cu(HO)}_2(\text{crystalline}) \\ \text{Cu}_2\text{O} \end{array} \right. N\text{-NaOH} = -0.074 \text{ volt.}$$

$$\text{Pt} \left| \begin{array}{l} \text{stabilised CuO} \\ \text{Cu}_2\text{O} \end{array} \right. N\text{-NaOH} = -0.154 \text{ volt.}$$

$$\begin{aligned} \text{The change } [\text{Cu(HO)}_2] &\rightarrow [\text{CuO}] + [\text{H}_2\text{O}] \\ &\quad \text{(Crystalline)} \quad \text{(Fresh)} \quad \text{(Liquid)} \\ \text{absorbs } 96540 \times [0.068 - (-0.074)] &\text{ joules} \\ &= 96540 \times 0.142 \\ &= 13700 \text{ joules.} \end{aligned}$$

$$\begin{aligned} \text{The change } [\text{Cu(HO)}_2] &\rightarrow [\text{CuO}] + [\text{H}_2\text{O}] \\ &\quad \text{(Crystalline)} \quad \text{(Stabilised)} \quad \text{(Liquid)} \\ \text{gives out } 96540 \times [-0.074 - (-0.154)] &\text{ joules.} \\ &= 96540 \times 0.08 \\ &= 7720 \text{ joules.} \end{aligned}$$

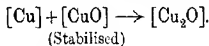
If, however, the stabilised copper oxide is prepared directly from the cupric hydroxide, fresh solid cupric oxide, not an aqueous solution, being the intermediate stage, we are dealing with two successive reactions: (a) reversible formation of fresh $[\text{CuO}]$, absorbing 13700 joules, and (b) irreversible formation of stabilised $[\text{CuO}]$, giving out 21420 joules; and dehydration cannot set in except when the aqueous vapour pressure of the system is kept below 0.1 mm. Then it will take place very slowly, its rate being determined by that of the reaction:



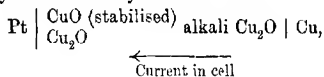
When, however, the change $\text{Cu(HO)}_2 \rightarrow \text{CuO(stabilised)} + \text{H}_2\text{O}$ has

an opportunity of taking place without the intermediate formation of "fresh" cupric oxide, it will set in. This will happen, for example, if the cupric hydroxide is treated with some solvent, such as an ammoniacal or alkaline solution, when the rate of reaction will depend on the concentration of the electrolyte, increasing with it. The saturated solution of cupric hydroxide is unsaturated with respect to the non-polymerised "fresh" cupric oxide, but supersaturated with respect to the polymerised "aged" cupric oxide, and this will settle out.

From the data contained in this paper and in the author's previous publication, we can calculate the free energy of the reaction:



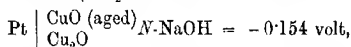
If one faraday is furnished by the combination



the total chemical effect will be given by the above equation.

Now we know that $\text{Cu} \mid \text{Cu}_2\text{O} \text{ N-NaOH} = -0.341$ volt

and



therefore the *E.M.F.* of the above combination is 0.190 volt, and the free energy change of the reaction concerned

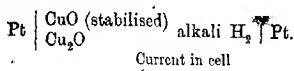
$$\begin{aligned} & 96540 \times 0.19 \\ & \hline & 4.19 \\ & = 4370 \text{ calories.} \end{aligned}$$

The total energy of the same reaction, calorimetrically determined, is 3600 cal. It should be noticed that, whereas the free energy change is deduced for cupric oxide which has become stabilised at the ordinary temperature, the value of the total energy change used holds for copper oxide which was very probably not stabilised when worked with. The two values are therefore not strictly comparable. It is not, however, likely that the irreversible molecular changes due to polymerisation or depolymerisation at constant temperature are bound up with changes of any magnitude in the total energy of the substance concerned.

This view is borne out by the fact that it is possible to calculate with considerable accuracy the dissociation pressure of cupric oxide at high temperatures from electromotive measurements carried out at the ordinary temperature (see the ensuing calculations), making use of the calorimetrically determined value of the total energy change, and assuming it to be constant over the whole temperature range. By the author's conception, the molecular complexity of the cupric oxide

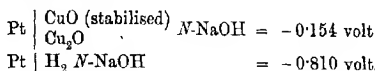
is supposed to change essentially with the alteration in temperature. If this is accompanied by any marked change in total energy, such calculations would not be possible.

Let us next consider the element



It can be regarded as a $\text{H}_2\text{-O}_2$ cell in which hydrogen at atmospheric pressure combines with oxygen furnished at the dissociation pressure of cupric oxide at the temperature in question, and from our data we can calculate this dissociation pressure.

We know that, at 17° ,



Hence the *E.M.F.* of the above cell at 17° is 0.656 volt.

Putting the *E.M.F.* of the $\text{H}_2\text{-O}_2$ cell at 17° at 1.232 we get:

$$0.656 = 1.232 + \frac{0.058}{4} \log p_{\text{O}_2}$$

whence $\log p_{\text{O}_2} = -39.7 = 40.3$, and p_{O_2} at 17° for $4\text{CuO} \rightarrow 2\text{Cu}_2\text{O} + \text{O}_2$, $= 2 \times 10^{-40}$ atmospheres.

By the use of the simple formula (26) given on p. 69 of Haber's *Thermodynamics of Technical Gas Reactions*, we can also calculate the dissociation pressures of cupric oxide at higher temperatures.

Putting in $A=0$, $T=290^\circ$, $R=2$, $Q=67200$, $\log p_{\text{O}_2} = -39.7$, we get: $k = -48.9$.

If we now extrapolate to 1030° (1303° abs.), we obtain $\log p_{\text{O}_2} = 1.42$,

$$\begin{aligned} \text{or } p_{\text{O}_2} \text{ at } 1030^\circ \text{ for } 4\text{CuO} \rightarrow 2\text{Cu}_2\text{O} + \text{O}_2 \\ &= 0.26 \text{ atmosphere} \\ &= 200 \text{ mm.} \end{aligned}$$

Experimental determinations by Wöhler and Frey (*Zeitsch. Elektrochem.*, 1909, 15, 34) and by Foote and Smith (*J. Amer. Chem. Soc.*, 1908, 30, 1344) give 170–180 mm. at 1030° . The coincidence falls within the limits of experimental error as far as the electrometric measurements are concerned, and is much better than could be expected, taking into consideration the approximate nature of the calculation involved. This agreement affords additional support to the correctness of the figure -0.154 volt for the equilibrium value at 17° of the electrode potential $\text{Pt} \left| \begin{array}{c} \text{CuO} \\ \text{Cu}_2\text{O} \end{array} \right| N\text{-NaOH}$.

If, on the other hand, we calculate the dissociation pressure of cupric oxide at the two temperatures mentioned from purely thermal data by means of Nernst's well-known formula :

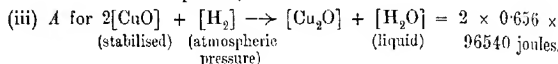
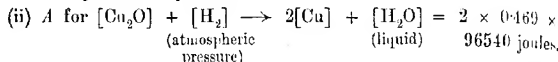
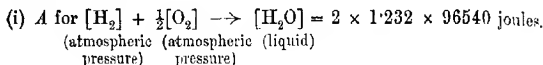
$$(\log_2 p_{O_2} = \frac{-Q}{4.57 T} + 1.75 \log T + 2.8),$$

we get at 170° : $p_{O_2} = 2.5 \times 10^{-44}$ atmosphere

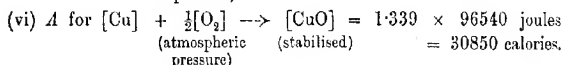
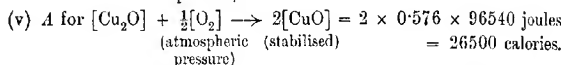
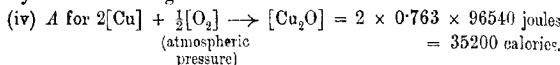
at 1030° : $p_{O_2} = 0.66$ mm.

In both cases the values are far too low, but the discrepancy is considerably greater at room temperature than at 1030° .

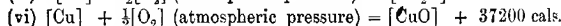
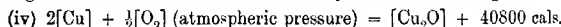
We can also calculate the free energy changes (A) for several other reactions. We know that at 17° :



By subtraction we get :



With (iv) and (vi) we can compare the corresponding total energy changes. These have been calorimetrically determined, and gave:



In conclusion, a few remarks may be made concerning a phenomenon noticed by Wöhler in his studies of the thermal dissociation of oxides of copper, palladium, platinum, and iridium (*Ber.*, 1903, 36, 3475; *Zeitsch. Elektrochem.*, 1905, 11, 836; 1906, 12, 781; 1908, 14, 97; 1909, 15, 34). It was sometimes observed that the equilibrium oxygen pressure of a sample of oxide kept at constant temperature did not remain constant, but gradually fell. As the oxides in question were partly decomposed under the conditions of measurement, he attributed this drop in pressure to solid solution formation setting in between the still undecomposed oxide and its solid reaction product. The probability of this explanation being the true one cannot be gainsaid,

but some of his experiments on cupric oxide were also carried out with samples of material which were kept under an excess oxygen pressure until the first reading was taken, and where very little opportunity of cuprous oxide formation was consequently presented. In spite of that fact, high initial values which rapidly fell were noticed, and these values did not represent states of equilibrium as the later ones obtained did, that is to say, if the pressure were slightly increased or decreased, it did not adjust itself again to its original value. Wöhler attributed these pressure changes also to solid solution formation, due to the minimal amounts of cuprous oxide produced, in which case the dissociation pressures of pure cupric oxide would lie higher still. It is quite possible, however, that they may be due to two other causes, as follows:

(1) High initial dissociation pressures given by the finest of the copper oxide particles present. In two samples of oxide microscopically examined by the author, one, prepared from copper nitrate, proved to have a large number of particles down to $1-2\mu$ in size, and the other, made from copper hydroxide by dehydration with ammonia at 25° , consisted to a great extent of particles of dimensions less than 0.5μ . In both cases the solubility in aqueous solutions of the particles would be affected by their size; and Schoch (*Amer. Chem. J.*, 1903, **29**, 319) has further shown, experimentally, that the initial dissociation pressure given by yellow mercuric oxide, with its large proportion of very finely-divided material, greatly exceeds for that reason the pressures given by the red oxide, or by the yellow oxide which has been heated for some time.

(2) According to the conception which has been used to explain the experimental results of this paper, freshly prepared copper oxide will always contain an excess of the less complex molecules, and will therefore have a higher dissociation pressure than a copper oxide in which the different molecular species have come to equilibrium. This circumstance may be the cause of the lowerings of pressure mentioned.

It is also possible that the same cause may bring about the very rapid fall of the initial dissociation pressure which was sometimes noted by Wöhler during his experiments with iridium dioxide. They were ascribed by him to the presence of the unstable iridium sesquioxide.

In any case, isolated examples apart, the variations in potential shown by an electrode system containing samples of copper oxide which have been subjected to varying thermal treatment must, undoubtedly, have their counterpart in variations in oxygen dissociation pressures determined at higher temperatures; and under suitable experimental conditions, there is no doubt that such effects could be

isolated and studied. If not avoided, they will certainly seriously affect dissociation and affinity measurements, although less so than at low temperatures, owing to the more rapid setting up of equilibrium.

It will perhaps be objected that the possibility of solid solution formation is not excluded from the author's measurements. The likelihood of such a complication is very small. None of the copper oxides worked with could be affected before measurements were started—they were never heated above 1000° , at which temperature their dissociation pressure is less than 100 mm., and particular care was taken thoroughly to ignite those samples which were made from cuprous oxide. We should need some positive evidence before admitting the possibility of the formation of solid solution during the measurements, at such a low temperature, and with the very small Cu^{++} and Cu^{+} ionic concentrations in the electrolyte. Moreover, the different initial values given by different samples of oxide would not be thereby explained.

Summary of Results.

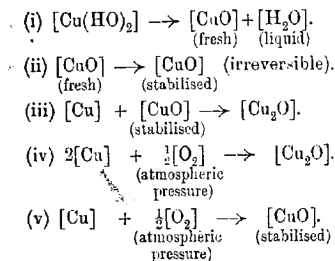
(1) Freshly prepared cupric oxide ages with time, and its free energy content thereby falls.

(2) This ageing is attributed to increasing molecular complexity, not to crystallisation or to surface changes.

(3) The explanation given accounts qualitatively for the electromotive behaviour of samples of copper oxide which have been subjected to varying thermal treatment, and may perhaps cast some light on phenomena noticed in the determination of dissociation pressures of certain oxides at higher temperatures.

(4) By means of tensimetric and electrometric measurements, it has been shown that crystalline cupric hydroxide is stable with respect to freshly prepared cupric oxide, and unstable with respect to old samples of cupric oxide.

(5) The decreases of free energy involved in the following reactions have been measured or calculated for 17° .



(6) The dissociation pressure of cupric oxide at 1030° has been calculated and found to agree satisfactorily with experimental results.

The author wishes, in conclusion, to offer his sincere thanks to Professor Donnan for advice and criticism received during the progress of this work.

MUSPRATT LABORATORY,
UNIVERSITY OF LIVERPOOL.

LXII.—*Solubilities Below and Above the Critical Temperature.*

By DAN TYLER.

It was first observed by Hannay and Hogarth in 1879 (*Chem. News*, 40, 256) that a solution of a salt, when heated to a temperature above the critical point of the solution, does not necessarily deposit the dissolved salt on the disappearance of the liquid phase. They showed; for example (*Chem. News*, 1880, 41, 103) that a solution of potassium iodide in ethyl alcohol could be heated to a temperature of about 100° above the critical temperature of the solution without the deposition of the dissolved salt.

Pictet (*Compt. rend.*, 1895, 120, 26) heated solutions of borneol, cineol, and terpineol in ether to temperatures above the critical point without the precipitation of any of the solute.

P. Villard (*Chem. News*, 1898, 78, 297, 309) found that easily volatile solids, like iodine and camphor, will dissolve appreciably at the ordinary temperature in compressed gases, such as oxygen and methane.

Centnerszwer and Tetelow (*Zeitsch. Elektrochem.*, 1903, 9, 799) have made some interesting experiments on the solution of anthraquinone in liquid sulphur dioxide; they found that if a certain quantity of anthraquinone is heated in a sealed tube with a particular quantity of liquid sulphur dioxide, the following phenomena occur:

- (1) The liquid expands and then diminishes in volume, owing to evaporation, until all the liquid just disappears at temperature t_1 .
- (2) As the temperature rises further, the quantity of anthraquinone left undissolved diminishes, and then liquid reappears at temperature t_2 .
- (3) The solid anthraquinone passes entirely into solution in the liquid at temperature t_3 .

(4) The liquid phase finally disappears at temperature t_c .

Obviously in the above, the solubility of the anthraquinone in the vapour of the sulphur dioxide increases with rise of temperature. Centnerszwer and Tetelow made a few measurements of solubility in a mixture of the liquid and vapour of the sulphur dioxide, but the results are not of much interest here. The solubility would be due to a large extent to the mere mechanical mixing of the vapour of the anthraquinone with the sulphur dioxide.

The above experiments show clearly that the phenomenon of solution is not peculiar to the liquid state, but, under certain conditions, the vapour of a liquid may dissolve solids in the same manner as a liquid solvent.

As no quantitative measurements of such solubilities seem to exist, it appeared to be of interest to make some determinations. In commencing this work I had the following objects in view:

(1) To determine the solubility of some non-volatile salts in liquid solvents from the ordinary temperature to the critical point.

(2) To continue the solubility curve through and beyond the critical point, and to find if there were any discontinuity at the critical point.

(3) To determine the solubility in the vapour above the critical point under different conditions of temperature and density of the solution.

Method of Experiment.

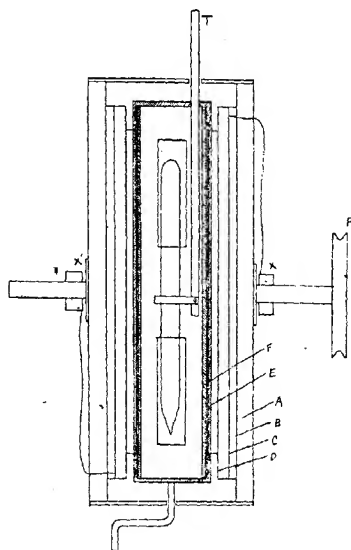
There seems to be only one practicable method of determining solubilities at high temperatures near the critical point. This method is the indirect one of starting with a mixture of the solvent and solute in known proportions and determining, by slowly raising the temperature, the minimum temperature of complete dissolution. Obviously this method is most accurate when there is a moderate change of solubility with change of temperature, and least accurate when this change is very small. The efficiency of the method does, of course, depend largely on the general efficiency of the apparatus and details of working.

Apparatus.

The sealed tubes containing the mixture of solute and solvent were heated in a specially constructed, electrically heated air-bath. This consists (see Fig. 1) of a series of cylinders, *A*, *B*, *C*, and *D*, made of sheet-iron. The cylinder *C* is wrapped closely with thin iron wire (diameter 0.5 mm.), which conducts the current and heats the bath. It is insulated from the metal cylinder by a wrapping of asbestos paper. The heat radiates first to cylinder *F*, and then to a thick ($\frac{1}{4}$ inch) iron cylinder *E*, in which fits closely, but loosely, another iron cylinder

F , of the same material. Through all the cylinders are cut two pairs of opposite windows. By the handle at the side, the innermost cylinder, F , can be turned and the windows shut off. This serves the double purpose of keeping the temperature in the interior more uniform, and also of protecting the apparatus from damage by a bursting tube. On to the ends of the cylinder, F , can be screwed thick iron caps, through one of which passes a thick iron tube, T , which carries a thermometer. The sealed glass tubes are held in the interior by a clip to the tube T ,

FIG. 1.



and the ends of the sealed tube are visible through the windows. The tube T can, moreover, be raised or lowered by a screw, and thus any portion of the sealed tube brought into view. To prevent external loss of heat as much as possible, the space between cylinders A and B is packed with asbestos wool, and the windows in these cylinders are fitted with panes of glass. The terminals of the heating wire are brought to two insulated copper cylinders, X , X' , forming sliding contacts with thick brass wires through which the current is brought. The ends of the outermost cylinder, A , are covered by sheet-iron

plates, to which are fastened disks of asbestos board. The whole apparatus is mounted on stands, and rotated on the pivots by means of a small motor attached by a rope to the pulley *P*. This serves the double purpose of agitating the liquid and salt inside the sealed tube, and of destroying convection currents of air in the interior of the bath and thus ensuring uniformity of temperature.

This bath gives very good results. By varying the external resistance to the current, the temperature can be varied from the ordinary temperature to 400° , or can be maintained constant for any length of time to 0.1° at low temperatures and to about 0.3° at high temperatures (350°).

The sealed tubes were made from glass tubing, the thickness of the walls of which varied from about 2.0 mm. to 4 mm. The capacity of the tubes was, on the average, about 30 c.c. The strength of sealed tubes depended largely on good clear glass free from surface scratches, and, of course, on the thickness and diameter. Tubing more than 4 mm. thick, and of a moderate diameter, was inconvenient to work in the blow-pipe flame.

The thermometers used were mercury thermometers reading to 0.1° , but at high temperatures it was not found practicable to read to less than 0.25° . They were carefully graduated by comparison with a standard thermometer.

It was found necessary in preparing the tubes to introduce particular quantities of the solvent and solute, so as to give a particular percentage concentration when saturated. Direct weighing of the solvent became, on this account, impracticable, and the solvent was, therefore, run out of a very carefully graduated burette consisting of a narrow tube with capillary exit-tube, which could be projected into the open end of the tube that was being prepared. In reading the volume of the solvent added, correction was made for room temperature.

Sodium Iodide and Ethyl Alcohol.

The sodium iodide was purified in the ordinary way by recrystallisation from a mixture of distilled water and alcohol. The last traces of moisture were removed by placing the partly dried salt in a bulb-tube and heating in a current of air until constant in weight.

The ethyl alcohol was commercial "absolute" alcohol, from which the last traces of water were removed by repeated treatment with sodium followed by fractional distillation. In order to prove that no reaction took place between the sodium iodide and the alcohol at a high temperature, a solution containing a known weight of sodium iodide was heated in a sealed tube to 300° for several hours. After cooling, the contents of the tube were analysed, when the original quantity of sodium iodide was found to be present.

The sealed tubes were prepared as follows : A selected piece of glass tubing was carefully and thickly sealed at one end, and drawn out to a narrow constriction a few inches from the other end. The capacity of the tube was then ascertained by running in mercury from a burette to a point in the constriction where the tube was subsequently sealed off. The tube was then cleaned and dried, and the requisite amount of sodium iodide added from a weighed bulb-tube having a long tube as neck, which was projected into the open end of the tube being prepared. To prevent an explosion in the tube between the air and the alcohol vapour when sealing off, the air was displaced by dry carbon dioxide. As a rule, the tubes were not evacuated, except those heated to the higher temperatures. The presence of a small quantity of carbon dioxide was found, by blank experiments, not to affect the solubility to any measurable extent. The requisite amount of alcohol was then added from the burette, and the tube then sealed off at a point in the constriction.

In preparing a tube for a determination of the solubility in the liquid at a high temperature, where the density of the vapour is quite appreciable, it was necessary to add such an amount of alcohol that by thermal expansion the amount of liquid existing in the state of vapour at the temperature of the determination would be negligibly small.

To a certain point it was found that the solubility increased with rise of temperature, and in determining a minimum temperature of dissolution within this range, the temperature was first raised quickly and a rough idea of the dissolution temperature obtained. Then the tube was cooled to about five degrees below this point, and raised very slowly with constant rotation of the bath until the point was found at which the last trace of salt just dissolved. The whole experiment required, on the average, between four and five hours.

At a higher temperature the solubility was found to decrease with rise of temperature, and in this case the temperature was raised quickly until some salt separated from the solution. The temperature of dissolution was then found as before, but by cooling instead of heating.

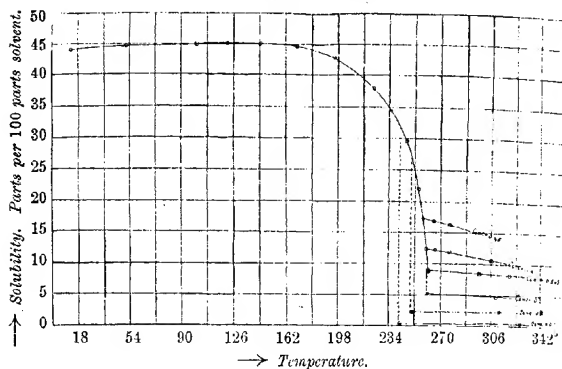
If the amount of alcohol added exceeded a certain critical quantity, then before the critical temperature was reached the solution expanded and filled the tube completely. At this point there was a break in the curve and a new curve began. Similarly, if the amount of alcohol added fell short of this critical quantity, the liquid would diminish in quantity, and, finally, all be vaporised before the critical point was reached. Again, there was a break in the solubility curve, and a new curve of solubility in the vapour began.

Results.

The numerical results of the solubility of sodium iodide in liquid alcohol from the ordinary temperature to the critical point are given in the following table. The values are calculated from a carefully drawn and smoothed curve of the experimental results, which are indicated in Fig. 2.

FIG. 2.

Solubility of sodium iodide in ethyl alcohol from ordinary temperature to temperatures above the critical point.



Solubility of Sodium Iodide in Liquid Ethyl Alcohol from the Ordinary Temperature to the Critical Point.

Solubility. Parts by weight of sodium iodide dissolved in 100 parts of ethyl alcohol.		Solubility. Parts by weight of sodium iodide dissolved in 100 parts of ethyl alcohol.	
Tempera- ture.		Tempera- ture.	
10°	43.77 ± 0.04	220°	38.5 ± 0.3
30	44.25 ± 0.10	230	36.2 ± 0.4
50	44.50 ± 0.05	240	32.7 ± 0.4
80	45.0 ± 0.1	250	26.2 ± 0.5
100	45.1 ± 0.1	255	21.0 ± 0.8
120	45.2 ± 0.1	260	10.8 ± 0.8
160	45.0 ± 0.2	261.5	8.6 ± 0.05
180	44.3 ± 0.2	(Critical temperature of solution)	
200	42.3 ± 0.3		

The probable accuracy of the numbers is appended. From 250° to 261.5° there is an enormous fall in the solubility, and the accuracy of the determinations in this range is much impaired on this account. The point at which the meniscus of a saturated solution just dis-

appears is 261.5° . This, it will be noticed, is very considerably higher than the critical point of the pure solvent. On reference to the curve (Fig. 2) it will be noticed that the solubility increases with rise of temperature to about 140° , and then decreases, at first slowly and then more rapidly, until the curve becomes almost vertical. At 261.5° the liquid phase ceases to be distinguishable from the vapour, and here there is a break in the solubility curve. This discontinuity is more apparent than real, as will be pointed out later. In order to show the phenomenon of the slow disappearance of the meniscus, a tube of given volume must contain approximately a definite amount of solvent. The amount of solvent contained in a tube of given volume is expressed in terms of the concentration of the solvent when all the liquid has disappeared, that is, the amount of solvent contained in unit volume. The critical concentration was found to be 0.365, but this figure is only approximate, as the point is very indistinct, concentrations of 0.370 and 0.360 both giving the critical phenomenon of the slow disappearance of the meniscus. If the concentration of the solvent exceeds 0.365 gram per c.c., the liquid will expand and fill the tube entirely. If the concentration of the solvent is, for example, 0.45 gram per c.c., the saturated solution will just fill the tube completely at 255° , and at this point there is a break in the curve, and, on continuing, the almost horizontal curve indicated is obtained. Similarly, a solution of concentration of the solvent of 0.4 gram per c.c. fills the tube completely at 259° , and another curve branches out, which it will be noticed has a smaller gradient than that of concentration 0.45. The critical curve of concentration 0.365 slopes still less. If now the concentration of the solvent is below the value 0.365, the liquid boils away before the critical point is reached. If, for example, the concentration is 0.1 gram per c.c., the liquid just completely evaporates at 242° , and then there is a drop in the solubility from 31.9 per cent. in the liquid to about 0.5 per cent. in the vapour. Temperature up to about 325° has no measurable influence on the solubility in the vapour of this particular concentration. A solution of concentration of the solvent of 0.2 gram per c.c. also gives a curve parallel to the abscissa; the curve of concentration 0.3 has a very slight gradient.

The numerical results of the solubility in the vapour at varying conditions of temperature and concentration are given in the following table. The numbers express parts by weight of sodium iodide which dissolve in 100 parts of ethyl alcohol.

Solubility of Sodium Iodide in the Vapour of Ethyl Alcohol above the Critical Point.

Temperature.	Concentration of the Solvent.						
	0.1	0.2	0.3	0.365	0.4	0.45	0.48
262°	0.5±0.1	2.1±0.1	5.1±0.05	8.6±0.05	11.6±0.1	17.3±0.2	21.6±0.4
270	"	"	5.1	8.35	11.5	17.0	—
280	"	"	5.0	8.2	11.0	16.5	—
290	"	"	4.9	8.0	10.5	—	—
300	"	"	4.8	7.7	10.2	—	—
310	"	"	4.7	7.5	9.7	—	—

The above figures are calculated from the smoothed curves of observed results. The probable accuracy in the first series at 262° is appended. The accuracy of the remaining numbers is only comparative, that is, it depends on the accuracy of the first series.

Determinations in the vapour were very difficult to make. Owing to the homogeneity of the solvent above the critical point, the mixing of the solvent and solute was less efficient than in the liquid state, where the solvent was not wholly homogeneous. The salt had, moreover, a peculiar aptitude for crystallising on the sides, but this difficulty was largely overcome by placing in the tubes small pieces of platinum foil, which, falling up and down the tube, assisted the dissolution. It was found that the process of dissolution in the vapour was much accelerated by keeping the temperature at the point at which the liquid disappeared, so that the undissolved salt remained moist, and the saturated liquid solution would completely evaporate without deposition of the dissolved salt. The following way of testing whether the solution in the vapour was saturated or not proved very useful. If the bath were kept vertical for a short time, the upper part of the tube would become slightly hotter than the lower part, with the result that the vapour within the tube would expand locally, and, if saturated, would deposit a thin, crystalline film of salt on the sides of the hotter portion of the tube. Indeed, it was possible in this manner to distil the solid salt from one portion of the tube to another. It was found impossible to continue the determinations above about 310°, for, in order to ensure a fair degree of accuracy, it was necessary to use fairly large tubes, so as to hold moderate amounts of the solvent and solute, and with increase in size of the tube, the strength decreased.

The curve of solubility in the vapour at 262° showing the relation between solubility and concentration of the solvent is given in Fig. 3.

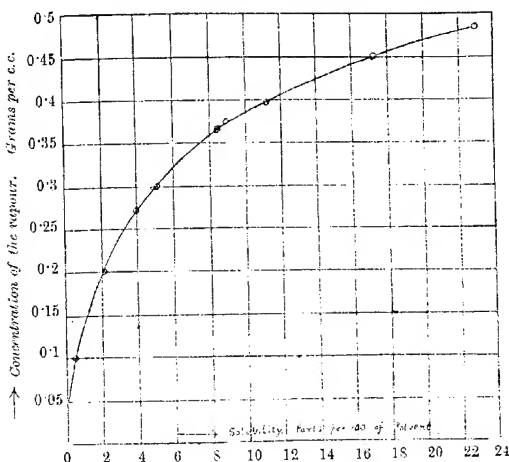
It will be noticed that the solubility diminishes regularly with decrease of concentration, becoming practically zero at a concentration of about 0.05 gram per c.c.

Potassium Iodide and Methyl Alcohol.

The potassium iodide was purified by recrystallisation, and completely freed from traces of moisture by heating in a bulb-tube in a current of air until constant in weight. The methyl alcohol was the commercial "absolute" alcohol, which was freed from last traces of

FIG. 3.

Solubility curve of sodium iodide in vapour of methyl alcohol at 262°.



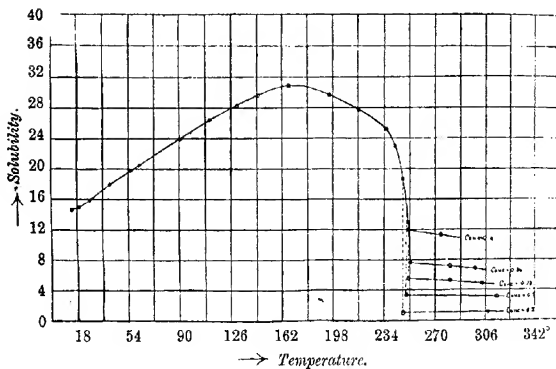
water by keeping it over excess of anhydrous copper sulphate for a fortnight, and then fractionally distilling. A sample, kept for months afterwards in a sealed tube with a little anhydrous copper sulphate, did not affect the colour of the latter, although it dissolved a little to a blue solution. The general method of investigation was the same as in the previous case, and it is only necessary to give here the numerical results and curves. No reaction was found to take place between potassium iodide and methyl alcohol even at 300°.

Solubility of Potassium Iodide in Liquid Methyl Alcohol from the Ordinary Temperature to the Critical Point.

Tempera- ture.	Solubility, Parts per 100 of methyl alcohol.	Tempera- ture.	Solubility, Parts per 100 of methyl alcohol.
15°	14.50 ± 0.05	200°	29.1 ± 0.2
30	16.20 ± 0.05	220	27.5 ± 0.2
50	18.9 ± 0.06	240	24.8 ± 0.3
80	22.55 ± 0.08	245	22.6 ± 0.5
100	25.0 ± 0.1	247	21.0 ± 0.5
120	27.2 ± 0.1	250	13.8 ± 0.6
140	29.2 ± 0.15	252.5	7.6 ± 0.1
160	30.6 ± 0.2	(Critical temperature of saturated solution)	
180	30.7 ± 0.2		

FIG. 4.

Solubility curve of potassium iodide in methyl alcohol from ordinary temperature to 310°.



The above figures are calculated from a smoothed curve of experimental numbers. The probable accuracy is appended. The critical concentration of the solvent was found to be about 0.36, but this point is even more indistinct than in the previous case. The above results are shown graphically in the curve in Fig. 4. It will be seen that the solubility first increases to about 170° and then decreases. The rate of decrease during the range 240—250° is exceedingly great. The rest of the curve will be easily understood from the explanation given in the case of sodium iodide and ethyl alcohol.

The numerical results for the solubility in the vapour are given in the following table.

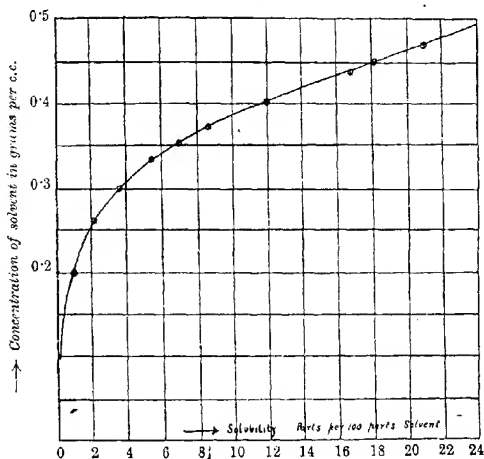
Solubility of Potassium Iodide in Vapour of Methyl Alcohol above the Critical Point.

Temperature.	Concentration.					
	0.1	0.2	0.3	0.36	0.4	0.45
252°	<0.3	1.0±0.05	3.7±0.1	7.6±0.1	11.8±0.1	18.1±0.2
270	—	„	3.5	7.4	11.5	—
280	—	„	3.4	7.3	11.3	—
290	—	„	3.4	7.2	11.0	—
300	—	„	3.3	7.0	—	—

The above figures represent the solubility in parts by weight dissolved in 100 parts of the solvent.

The accuracy of the numbers beyond the first series is dependent on

FIG. 5.



the accuracy of the numbers in the first series; the relation between the solubility in the vapour at 252° and the concentration of the solvent is shown in the curve in Fig. 5. The curve is similar to that obtained in the case of sodium iodide and ethyl alcohol.

Discussion of Results.

The first and most interesting point to notice is that the solubility in the vapour is a function of concentration of the solvent. An extension of this idea to the liquid state explains the very great and

rather sudden fall of solubility in the liquid just below the critical temperature. For over this range the rate of expansion of the solution is very much greater than at lower temperatures. It also explains the apparent discontinuity in the solubility curve at the critical point, for just previous to the critical point the solvent has been undergoing a great decrease in concentration, and when this point is reached this decrease, of course, stops and the concentration of the solvent remains practically constant (the slight expansion of the glass being neglected), with the result that the solubility remains nearly constant. If we imagined the concentration of the solvent to decrease past the critical point at the same rate as before, and if we plot the solubilities for the concentrations thus obtained, we get no discontinuity at the critical point, but a perfectly uniform curve.

The second point to notice is that the solubility in the vapour decreases with rise of temperature, although the concentration remains constant, and, further, that this decrease is greater for the greater concentrations of the solvent. This would suggest the formation of hydrates in the solution which dissociate under the influence of heat. If the process of solution is due to an attractive force between the molecules of solute and solvent, then we should expect, as is here found to be the case, that the solubility at constant temperature would vary directly with the concentration of the solvent.

In conclusion, I desire to express my thanks to Prof. H. B. Dixon and Dr. A. Lapworth for much kind advice and interest taken in the work.

THE CHEMICAL DEPARTMENT,
THE UNIVERSITY,
MANCHESTER.

LXIII.—*A Supposed Case of Stereoisomeric Tervalent Nitrogen Compounds.*

By HUMPHREY OWEN JONES and EDWARD JOHN WHITE.

IN 1896 (*Ber.*, **29**, 1462) von Miller and Plöchl described two isomeric compounds, $C_{12}H_{11}ON$, obtained by the interaction of *m*-4-xylydine and acetaldehyde in dilute hydrochloric acid solution: these differed in crystalline form, melting point, solubility, and stability. The more soluble and more fusible form, melting at 102° , hereinafter called the α -form, was partly converted into the β -form, melting at 131° , by crystallisation from solvents, by solution in acids, or by heat. Both compounds gave the same oxime, benzoyl

derivative, and condensation product; $(C_{10}H_{13}N)_2$, with xylidine, also the same 2:6:8-trimethylquinoline was obtained from both.

The two isomeric compounds were therefore considered to have the same structural formula, namely, $C_6H_3Me_3 \cdot NH \cdot CHMe \cdot CH_2 \cdot CHO$, and it was suggested that they differed only in the disposition of the three groups around the tervalent nitrogen atom.

It is remarkable that the observations on this interesting case of isomerism have not been extended, especially on account of its important bearing on the stereoisomerism of nitrogen.

The present paper contains a short account of a re-investigation of these compounds, and of the preparation of similar compounds from other amines.

The method of preparation has been improved, and it has been found that the properties of the compounds agree generally with those described by Miller and Plöchl, but with the important difference that *neither isomeride is transformed into the other by the action of solvents or of heat*. This fact renders the hypothesis of stereoisomerism untenable, but the nature of the isomerism is still a problem of general interest.

Although no transformation is effected by heat or inert solvents, it is brought about readily by the action of acids. In dilute acid solution the α - and β -forms are converted into the same equilibrium mixture, consisting of approximately two parts of the α - to one part of the β -compound, which is also the composition of the mixture obtained in the preparation of the substances in the first instance: this equilibrium mixture in acid solution changes into 2:6:8-trimethylquinoline, slowly at the ordinary temperature, and rapidly on heating.

In addition to yielding the same oxime, benzoyl derivative, and condensation product with xylidine, the two isomerides gave the same benzylphenylhydrazone and the same methyl derivative, $C_6H_3Me_3 \cdot NMe \cdot CHMe \cdot CH_2 \cdot CHO$.

The only difference in chemical properties which the two compounds have been found to exhibit is in their behaviour towards hydrogen chloride and towards nitrous acid. When a solution of the α - or β -compound in ether or benzene was treated with hydrogen chloride, a compound of the composition $C_{12}H_{17}ON, HCl$ was precipitated in each case; that from the α -form melts at 85° , whilst that from the β -form melts at 135 – 136° , and is identical with the product obtained by the action of aqueous hydrochloric acid.

The difference in the products of the interaction of the two compounds and nitrous acid is remarkable; both compounds yielded a non-basic substance which gave Liebermann's nitroso-reaction; but whereas the product obtained from the β -form was

crystalline and had the composition $C_{12}H_{19}O_2N_2$, that from the α -form was oily and could not be obtained pure.

The absorption spectra of the two forms have been examined, and the curves obtained are very nearly but not quite identical.

Similar isomeric compounds have been prepared from *p*-toluidine and ψ -cumidine.

As regards the cause of this case of isomerism, it is clear that the α - and β -compounds cannot be stereoisomeric, since each is too stable towards heat, and under the influence of solvents, and of two compounds differing only in the disposition of the groups around the tervalent nitrogen atom, one would inevitably be very unstable. Yet any structural difference between the compounds must be slight and easily removed, since so many derivatives are identical, and the absorption spectra are so nearly the same. In all cases the α -compound is distinctly more reactive than the β -compound, but in two cases only are the derivatives of the two isomerides different, namely, the hydrochlorides and nitroso-compounds.

The adoption of the formula $C_6H_5Me_2 \cdot NH \cdot CHMe \cdot CH_2 \cdot CHO$ for the α -compound, and

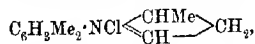


for the β -compound, affords a satisfactory explanation of all the facts observed, with the exception of the action of nitrous acid.

The hydroxytrimethyleneimine ring present in the β -compound would be unstable, especially towards acids, just as the trimethyleneimine ring has been found to be (Howard and Marckwald, *Ber.*, 1899, 32, 2031), and under the influence of acids or other reagents would undergo fission, so that the product obtained from the β -compound with hydroxylamine, benzoyl chloride, benzyl-phenylhydrazine, or methyl iodide would be identical with that obtained from the α -compound.

Certain suggestions might be made to account for the different products obtained by the action of nitrous acid, but the experimental evidence is insufficient to discriminate between them. Both compounds are insoluble in acids, so that it is improbable that either is an ester or a salt.

The products obtained with hydrogen chloride would be the simple additive products, different for the α - and β -forms: there is no evidence of the formation of an ammonium salt of the type



similar to that formed from cotarnine (Dobbie, Lauder, and Tinkler, *Trans.*, 1903, 84, 598).

EXPERIMENTAL.

The method given by Miller and Plöchl for obtaining the mixture of the two isomeric compounds consists in mixing xylydine, dilute hydrochloric acid, and acetaldehyde, keeping the mixture for one day, and then fractionally neutralising it. A dark resinous substance is first formed, and is removed, after which a red oil, representing the isomeric mixture, separates. This is extracted with ether, and the crystalline product is obtained from the ethereal solution after concentration, part of it by addition of light petroleum, and the remainder by keeping the gummy mother liquor for some days, when a further crop of crystals separates. In this way 20 grams of xylydine yield 17 grams of yellow, solid product.

Several difficulties were encountered in repeating the preparation as above described. There is no definite stage in the neutralisation of the acid solution to separate the resinous from the oily precipitates, and in reality a complicated succession of precipitates of different degrees of colour and consistency is obtained. Consequently, either the yield of solid product is small, owing to the greater part of the crystalline material having been removed along with the "resin," or less "resin" is separated and the crystalline material is only very slowly obtained from the impure ethereal solution. Moreover, in addition to the two crystalline, isomeric substances, and to the dark-coloured, uncrystallisable substance, which is probably ethylenexylydine, $C_6H_3Me_2N:CHMe$, a third crystalline substance is invariably present in the product, the so-called bimolecular ethylenexylydine, $C_{20}H_{26}N_2$. Miller and Plöchl seem to have overlooked its presence, but it is formed in considerable quantity, 20 grams of xylydine yielding about 4 grams, and of this amount a large proportion must inevitably have been present in their 17 grams of crude product.

It was found possible, however, by modifying the original method of preparation to overcome both difficulties simply and successfully, and thus obtain a better yield of the product as a white, crystalline solid. The modified process depends on the fact that both the coloured, uncrystallisable impurity and the bimolecular ethylenexylydine are soluble in light petroleum and dissolve very readily if the light petroleum is present at the time of their precipitation, whereas the isomeric substances are only very sparingly soluble in the cold solvent. The method is as follows.

Xylydine (10 grams) was poured into Erlenmeyer flasks containing twice the equivalent quantity of hydrochloric acid diluted with water to 120 c.c. A slight excess (11 c.c.) of acetaldehyde was

added, and the mixture kept in the stoppered flasks at the ordinary temperature for at least eighteen hours.* About 40 c.c. of light petroleum were now added, and the requisite amount of alkali for complete neutralisation was poured in quickly, the flask being vigorously shaken. The red petroleum solution contained the impurities, and after a few minutes the isomeric mixture separated as a white, crystalline cake on the surface of the water-layer. The solid product was collected, washed with light petroleum and water, and dried.

The crystalline mixture, 12 grams of which are thus obtained from 10 grams of xylydine, melts at 84–87°, and consists approximately of 8 grams of the α - and 4 grams of the β -isomeride. The composition in this and other cases is approximately deduced from the residue of β -compound left after extracting the more soluble α -compound from a weighed quantity of the mixture, allowance being made for the β -compound, which is removed at the same time.

Miller and Plöchl obtained the less soluble β -form by fractional crystallisation from ethereal solution and the α -form by mechanical separation. The following method was found much more suitable for the preparation of the β -compound. The amount of benzene required to dissolve the more soluble component was added to the mixture (60 c.c. of benzene for 12 grams of mixture), and after shaking for about half an hour, the solid residue was removed by filtration. After one recrystallisation from benzene, nearly 4 grams of pure substance were obtained.

The α -isomeride is very difficult to separate in a state of purity. The method of mechanical separation is unsuitable for obtaining large quantities of the pure substance. This is chiefly because neither compound shows much tendency to crystallise in large individual crystals. Various solvents were tried, and many modifications were made in the conditions of crystallisation and separation, but in every case only a very small proportion of each product consisted of separable crystals. Even under the most favourable conditions the crystallised mixture is mainly made up of masses which consist of radiating clusters of both kinds of crystals, and cannot be detached so as to admit of mechanical separation. For the same reason, although there is an appreciable difference of density, namely, 1.13 and 1.19 for the α - and β -forms respectively, the method of separating by means of a liquid of intermediate density was also unsuccessful. Since, as will be seen later, the α -form is not transformed by the action of inert solvents,

* Longer keeping than eighteen hours, even for several days, has no further influence on the nature or quantity of the products.

it should be possible to separate it by fractional crystallisation. Repeated crystallisation from various solvents never gave specimens with a higher melting point than 96—99°, whereas the pure α -compound melts at 103—104°. The explanation of this undoubtedly lies in the relative solubilities of the two compounds. The solubilities in various solvents, including benzene, ether, acetone, and alcohol, were determined, and it was found that, in each of these cases, the ratio between the solubilities of the compounds has very nearly the same value, namely, about 4:1. It follows that the more soluble component cannot be purified by a simple process of crystallisation until a solvent is found for which the two solubilities are either more nearly equal or more discrepant than they are in the above cases. The difficulty caused by this accidental uniformity in the relative solubility of the two isomerides has not yet been overcome. At present the only means of obtaining the pure α -compound is by mechanical separation followed by crystallisation; this is very slow and tedious, but enough of the pure α -compound has been obtained in this way to allow of an investigation of its properties.

Melting Point.—The melting points given by Miller and Plösch are 102° and 131° for the α - and β -compounds respectively. It is now found that the α -form melts at 103—104°, and the β -form at 127—128°. In both cases, especially the former, the melting point is much affected by the presence of impurity. It is noteworthy, in connexion with the question of transformability, that the melting point of individual rhombohedral crystals picked out from the crystalline mixtures is never more than 99—101°, and is usually considerably lower; therefore, after mechanical separation, the crystals of the α -compound must be recrystallised before the substance can be obtained quite pure.

Crystalline Form.—The crystals of the α -isomeride have commonly a rhombohedral appearance, but are often elongated, and are then not so easily distinguished from those of the β -form. The latter are flat needles, differing from the former in possessing marked cleavage, the cleavage fragments being diamond-shaped. Both kinds of crystals occur usually as radiating clusters of small individuals.

Solubility.—The α -compound is easily soluble in acetone, benzene, ether, or alcohol, these solvents being arranged in descending order of solubility. It is very sparingly soluble in cold, but moderately so in hot light petroleum, and insoluble in water. It is readily soluble in dilute acids. The solubility of the β -isomeride, as already stated, is in all these cases proportionately less, the ratio being very nearly constant at 1:4.

Absorption Spectra.—These were observed by Mr. J. E. Purvis, and are described in the paper following this. The curves for the two isomerides are very nearly but not quite identical. The spectra of the corresponding *p*-toluidine derivatives, the preparation and properties of which are described later, show very clearly a difference of precisely the same nature as that observed in the xylidine derivatives.

It is impossible to draw very definite conclusions from these results as to the constitution of the two compounds, but it is extremely probable that two substances, with absorption spectra so nearly the same, would only differ slightly in chemical constitution.

Transformability.—Miller and Plöchl state that the β -compound is stable, but that the α -compound is "partly" transformed into the other form by (i) simple crystallisation from solvents; (ii) keeping in acid solution for some time; (iii) heating above its melting point. It was found that no transformation could be effected either by solvents or by heat.

In addition to showing that the pure α -compound could be recrystallised several times without changing the melting point, the following more stringent experiments were made. Solutions of the purified substance, melting at 103–104°, in different solvents, such as benzene or light petroleum, were heated to 100° in sealed tubes for several hours, after which the substance was recovered absolutely unchanged.

The effect of heat alone was examined by heating the α -form in an air-oven to 110° (at higher temperatures quinoline formation takes place very rapidly). The substance was then washed with light petroleum in order to remove any trimethylquinoline which had been formed, and the residue again proved to be unchanged substance, melting at 103–104°.

The β -compound was submitted to the same treatment and found to be equally stable.

Action of Acids.—The two compounds are, however, transformed on treatment with acids. The α -form is much more easily dissolved by dilute hydrochloric acid than the β -form, but on keeping in acid solution each form is transformed into an equilibrium mixture, which has the same composition as the mixture obtained when the substances are prepared in the ordinary way by the condensation of xylidine and aldehyde in acid solution. In cold dilute acid the change is slow, needing several days for completion, but on warming the solution, the equilibrium is attained in a few minutes. In all cases when either the α - or the β -compound is dissolved in acid and reprecipitated by the addition of alkali, the

quantity of base recovered is considerably less than the amount dissolved, owing to the formation of 2:6:8-trimethylquinoline, which takes place very readily under the influence of acids.

Action of Hydrogen Chloride.—The α - and β -compounds were dissolved in dry ether or benzene, and dry hydrogen chloride was passed into the solution, when a white precipitate separated immediately.

The α -form yielded a deliquescent product, which sintered at 80°, and melted with frothing at 85°:

0.2755 gave 0.6345 CO₂ and 0.1910 H₂O. C=62.8; H=7.7.

0.2579 „ 0.1654 AgCl. Cl=15.8.

C₁₂H₁₇ON, HCl requires C=63.3; H=7.91; Cl=15.7 per cent.

The aqueous solution was acid to litmus, and on the addition of alkali an oil separated, which crystallised after some time. The crystals melted at 88°, and were a mixture of the α - and β -forms.

The β -form yielded a white, crystalline precipitate, which melted without decomposing at 135–136°, and could be recrystallised from alcohol or water unchanged. The same substance is produced by allowing a solution of the base in aqueous hydrochloric acid to evaporate spontaneously, when it separates in long, needle-shaped crystals:

0.2715 gave 0.6220 CO₂ and 0.1895 H₂O. C=62.8; H=7.8.

0.2855 „ 0.1865 AgCl. Cl=16.1.

C₁₂H₁₇ON, HCl requires C=63.3; H=7.91; Cl=15.7 per cent.

The aqueous solution, on the addition of alkali, deposited a crystalline solid, which melted at 125°, and consisted of the β -form.

Formation of Trimethylquinoline.—The action of heat or of strong acids is, as stated by Miller and Plöchl, to decompose the compounds with formation of 2:6:8-trimethylquinoline. Thus, if the α -compound is heated to 120° in an air-oven for half an hour and the residue distilled in a current of steam, a 50 per cent. yield of trimethylquinoline will be found in the steam distillate as large, crystalline plates, melting at 45–46°. The β -compound requires heating to 150° for about two hours to give a similar yield.

Acids, even when cold and not very concentrated, slowly effect the same transformation, and the change takes place completely if either of the compounds is warmed for a few minutes with concentrated hydrochloric acid. This effect of acids is also illustrated by the action of *d*-camphorsulphonic acid. Dry acetone solutions of the two bases were mixed with dry acetone solutions of *d*-camphorsulphonic acid, with the object of preparing the camphorsulphonates. A crystalline product separated in each case, melting after purification at 229–231°, but when examined

was found to be a camphorsulphonate, not of the original bases, but of 2:6:8-trimethylquinoline. If ether is added to the solution immediately after mixing, colourless crystals separate, which melt at a low temperature (about 103°), but these change rapidly into the camphorsulphonate of 2:6:8-trimethylquinoline.

Aldehyde Reactions.—Miller and Plöchl lay stress on the fact that both compounds reduce ammoniacal silver solutions, taking this as indicating their aldehydic nature. The silver reduction does actually take place, but in neither case so readily as that brought about by the simple amines, such as xylidine itself. The test, therefore, is valueless. Both compounds do, however, condense with hydroxylamine, benzylphenylhydrazine, and xylidine, and these condensations will now be described.

Condensation with Hydroxylamine.—The method of preparing the oximes described by Miller and Plöchl was found to give good results. Both compounds give a 60 per cent. yield of the same compound, which, when crystallised from alcohol, melted at 163–166°, Miller and Plöchl's value being 165°. As the analysis given in the original paper is somewhat unsatisfactory, the following analytical results are appended:

0.1785 gave 0.4570 CO₂ and 0.1450 H₂O. C=69.8; H=9.0.

C₁₂H₁₈ON₂ requires C=69.9; H=8.75 per cent.

Since the isomeric compounds are both transformed into a mixture in acid solution, attempts were made to condense them with free hydroxylamine in alcoholic solution. Under these conditions, however, no reaction occurred, and the unchanged bases were isolated.

Condensation with Xylidine.—Both substances can be condensed with xylidine by simply mixing calculated quantities in alcoholic solution, and heating on the water-bath in a sealed tube, or in a flask provided with a reflux condenser. The condensation product is very sparingly soluble in alcohol, and in about three hours, in the case of the α -compound, it separates out as a white, crystalline precipitate, the yield being about 25 per cent. of the theoretical. The β -isomeride gives an equal yield after about six hours' heating. This method of condensation is found considerably quicker and simpler than Miller and Plöchl's method of heating the reagents suspended in a large quantity of water and afterwards proceeding to isolate the condensation product.

The only information available with regard to this condensation compound, the so-called bimolecular ethyліденexylidine, is to be found in a short paragraph in Miller and Plöchl's paper (*loc. cit.*, p. 1467), therefore a few supplementary details are given here. The compound crystallises in isolated, flat, six-sided plates with

vitreous lustre, and melts at 144–145°; Miller and Plöchl give 147°. It is moderately easily soluble in cold light petroleum, thereby differing from the isomeric compounds; it is easily soluble in benzene, ether, or dilute acids, and very sparingly so in alcohol.

No analyses or molecular weight determinations for the condensation product appear to have been published, but it has undoubtedly the formula $C_{20}H_{26}N_2$, as the following results show:

0.2070 gave 0.6185 CO_2 and 0.1660 H_2O . $C=81.5$; $H=8.9$.

0.415, in 17.50 benzene, gave $\Delta t = -0.400^\circ$. M.W.=296.

$C_{20}H_{26}N_2$ requires $C=81.6$; $H=8.84$ per cent. M.W.=294.

Miller and Plöchl assume that the constitutional formula is $C_6H_3Me_2NH \cdot CHMe \cdot CH_2 \cdot CH \cdot N \cdot C_6H_3Me_2$. Its empirical formula shows it to be a bimolecular polymeride of the simple Schiff's base, $C_6H_3Me_2N \cdot CHMe$, and the method of preparation and general properties render the above constitutional formula *prima facie* probable.

In addition to the method of preparation described above, two other methods may be employed. It is formed along with the isomeric bases when xylydine is condensed with acetaldehyde in acid solution, as has already been mentioned, but it is most conveniently prepared by the direct condensation of xylydine with acetaldehyde in alcoholic solution. The calculated quantity of acetaldehyde is slowly added to an alcoholic solution of xylydine at 0°, when the product separates first as a red oil, but in a few minutes solidifies to a yellow mass, which is collected and purified by recrystallisation from alcohol.

The compound is readily soluble in dilute acids, but in acid solution it slowly decomposes into xylydine and the equilibrium mixture of the isomeric compounds, the reaction occurring in the first method of formation being thus exactly reversed. It would therefore appear that, in acid solution, there is an equilibrium between the three substances, bimolecular ethylenexylydine and the two α - and β -compounds.

Condensation with Benzylphenylhydrazine.—The compounds were dissolved in alcohol, calculated quantities of benzylphenylhydrazine added, and the solutions allowed to evaporate. Gummy residues were left, which crystallised after several days. After crystallising from alcohol, it was found that the same derivative, melting at 120–121°, was obtained from both compounds:

0.1597 gave 0.4725 CO_2 and 0.1148 H_2O . $C=80.6$; $H=7.98$.

$C_{15}H_{29}N_3$ requires $C=80.9$; $H=7.82$ per cent.

Reaction with Benzoyl Chloride.—The reaction with benzoyl chloride takes place readily on adding excess of benzoyl chloride to a benzene solution of either compound in presence of a large excess

of 10 per cent. sodium hydroxide solution. The mixture is shaken vigorously during the addition of the benzoyl chloride, and finally shaken until all the benzoyl chloride has disappeared. After two or three hours, a white, crystalline product separates and floats on the benzene solution, and represents a 72 per cent. yield of the benzoyl derivative, which, after crystallising from alcohol, melts at 149–150°. It is sparingly soluble in ether or benzene, and quite insoluble in dilute acids. On the latter account, the compound must be an imino- and not a hydroxy-derivative, since the basic character of the original substances has evidently been destroyed by the introduction of the benzoyl group.

Reaction with Nitrous Acid.—In this case the two compounds show a remarkable difference of behaviour. Both compounds, when dissolved in cold dilute hydrochloric or acetic acid and treated with potassium nitrite solution, gave precipitates which, after careful washing, gave Liebermann's test for nitroso-compounds. Both compounds would therefore appear to be secondary bases, but there is this difference. In the case of the α -compound the precipitate is a yellow, oily substance, which cannot be obtained crystalline, whilst the β -compound gives at once a faintly yellow-coloured, crystalline precipitate. The latter was recrystallised from ether and light petroleum, and obtained in plates, melting at 112–113°:

0.1100 gave 0.2635 CO_2 and 0.0715 H_2O . C = 65.3; H = 7.22.

$\text{C}_{12}\text{H}_{16}\text{O}_2\text{N}_2$ requires C = 65.45; H = 7.27 per cent.

Action of Methyl Iodide.—The α - and β -compounds react slowly with methyl iodide, forming sometimes a gummy substance, which afterwards becomes crystalline, and sometimes forming a crystalline product directly.

The products were readily soluble in alcohol, and appeared to be mixtures.

The aqueous solutions have an acid reaction, and on treatment with sodium carbonate or sodium hydroxide each compound yielded a small quantity of oily precipitate, which crystallised on keeping; this was readily soluble in ether, but very sparingly so in light petroleum. On repeated crystallisation from a mixture of ether and light petroleum, the products from the α - and β -compounds separated in fine needles, melted at 45–46°, and were apparently identical. It seems probable that this is the methyl derivative, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NMe}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CHO}$. This product resembles 2:6:8-trimethylquinoline in some respects, but the solubility in light petroleum discriminates between them, since the quinoline derivative is readily soluble in this solvent.

Other pure compounds have not been separated from the products

of the action with methyl iodide, but on repeated recrystallisation the melting point varied from 215° to 230° , and the composition was apparently that of a mixture. It is probable that in each case the product is a mixture of the methyl iodide additive compounds of 2:6:8-trimethylquinoline and of the tertiary base mentioned above, together with the hydriodide of the latter.

Analogous Compounds from other Amines.—Several amines, including aniline, *o*- and *p*-toluidines, *o*- and *p*-xylydines, and ψ -cumidine, were treated with acetaldehyde in acid solution in the same manner as *m*-4-xylydine. The precipitates obtained by neutralisation in presence of light petroleum varied considerably in appearance. In two cases, those of *p*-toluidine and ψ -cumidine, the precipitate was slightly coloured and crystalline, but the other amines gave products which were viscous and dark coloured. The products obtained from *p*-toluidine and ψ -cumidine were fractionally crystallised, and found to consist of mixtures of two isomerides corresponding with the α - and β -xylydine isomerides, along with compounds corresponding with bimolecular ethyldiene-xylydine. In the ψ -cumidine product, the latter derivative predominates, and it is probable that, with many of the other bases, the isomeric pairs of compounds only form a very small part of the product, the regular condensation product being the polymerised Schiff's base.

The β -compound isolated from the *p*-toluidine product consisted of small, colourless plates, melting at 164 – 167° , readily separated from the α -compound by crystallisation:

0.1570 gave 0.4265 CO_2 and 0.1185 H_2O . $\text{C}=74.1$; $\text{H}=8.38$.

$\text{C}_{11}\text{H}_{15}\text{ON}$ requires $\text{C}=74.57$; $\text{H}=8.47$ per cent.

The α -compound can be obtained by recrystallising the more soluble product and picking out the stout plates, which melt at 108 – 110° :

0.1673 gave 0.4555 CO_2 and 0.1295 H_2O . $\text{C}=74.23$; $\text{H}=8.60$.

$\text{C}_{11}\text{H}_{15}\text{ON}$ requires $\text{C}=74.57$; $\text{H}=8.47$ per cent.

From the cumidine product the derivatives isolated were:

The less soluble β -compound, melting at 110 – 112° :

0.2112 gave 0.5875 CO_2 and 0.0760 H_2O . $\text{C}=75.3$; $\text{H}=9.25$.

$\text{C}_{13}\text{H}_{19}\text{ON}$ requires $\text{C}=76.0$; $\text{H}=9.27$ per cent.

The α -compound melts at 80° .

The bimolecular Schiff's base, soluble in light petroleum, was also isolated, and melted at 160 – 161° . It closely resembles the corresponding xylydine compound in its properties:

0.1727 gave 0.5140 CO_2 and 0.1415 H_2O . $\text{C}=81.2$; $\text{H}=9.4$.

$\text{C}_{22}\text{H}_{29}\text{N}_2$ requires $\text{C}=81.98$; $\text{H}=9.3$ per cent.

These results show that the cause of the isomerism is not in any way connected with the benzene nucleus in *m*-4-xyldine, but is apparently general.

The expenses of this investigation have been defrayed by means of a grant from the Government Grant Committee of the Royal Society, for which we are glad to make this grateful acknowledgment.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

LXIV.—*The Absorption Spectra of p-Toluidine, m-Xyldine, and of their Condensation Products with Acetaldehyde.*

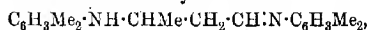
By JOHN EDWARD PURVIS.

WITH regard to the preceding investigations of Jones and White, it appeared to be of some interest to study the absorption spectra of the compounds they obtained in order (1) to compare the spectra with those of *p*-toluidine and of *m*-4-xyldine, and (2) to compare the spectra with each other so as to differentiate, if possible, the suggested linking of the nitrogen atom.

The absorption spectrum of *p*-toluidine has been examined by Hartley (Trans., 1885, 47, 685), and he found two bands in the dilutions he employed, one range being λ 3171— λ 2701, and the other λ 2568— λ 2310. The absorption curves have been investigated by the method and apparatus used by Purvis and Foster (Proc. Camb. Phil. Soc., 1908, 14, 381), and the results confirm Hartley's observations. It will be noticed (Fig. 1) that there are two bands, and that before the appearance of the band on the less refrangible side, the one on the more refrangible side of the spectrum disappears as the thickness of the solution increases.

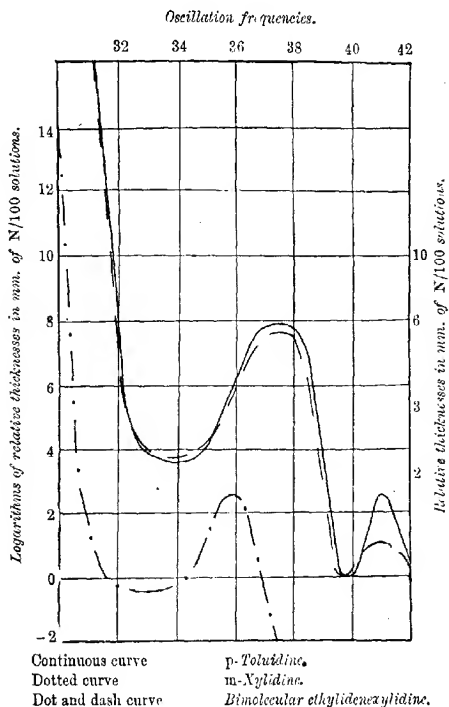
The spectrum of *m*-4-xyldine has not hitherto been studied, and from the absorption curve it will be seen that the bands are similar to those of *p*-toluidine. The differences are that the weighting of the molecule has produced a slight shift of the bands towards the red end of the spectrum, and also that the bands are not quite so persistent, the difference in this respect being greater for the more refrangible band.

The bimolecular ethylenexyldine (m. p. 144—145°), the constitutional formula of which may be written



was examined, and from the absorption curve (Fig. 1) it will be noticed that there has been a great shift of the band towards the red end of the spectrum, and that only one band was observed, the persistency of which was considerably diminished. The band on the more refrangible side occurring in *m*-4-xyldine was not

FIG. 1.

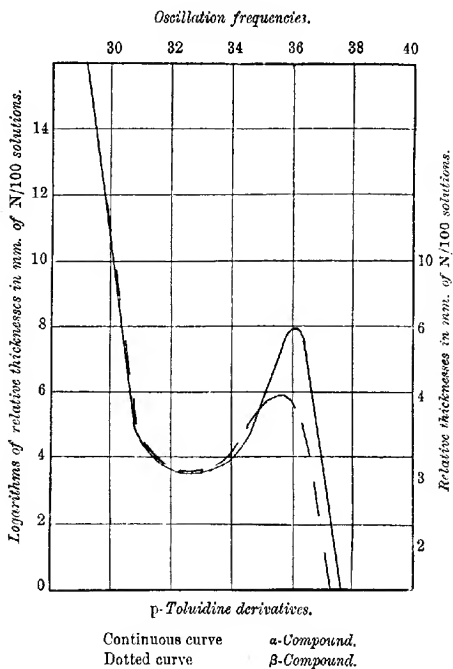


observed; and, although more diluted solutions of $N/1000$ and $N/10,000$ strengths were also examined, there were merely indications of this second band. The effect of the union of the two similar xyldine residues by the aliphatic group has been to reduce the persistency of the bands and not to destroy them.

The condensation product of *p*-toluidine and acetaldehyde

(α -form, m. p. 108—110°), $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CHO}$, was examined; and as regards the general form and persistency, the curve (Fig. 2) shows the presence of only one band, very similar to the band of *p*-toluidine on the less refrangible side of the spectrum. This band is shifted more towards the red end as a result of the

FIG. 2.



weighting of the molecule, and the second band on the more refrangible side has disappeared.

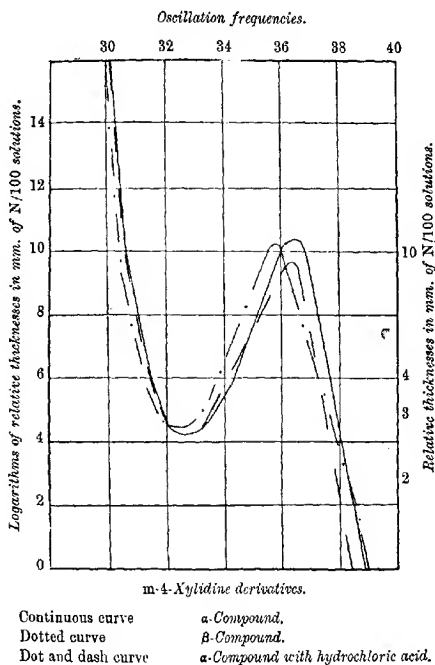
The corresponding β -compound (m. p. 164—167°), the suggested constitutional formula of which is:



was also examined, and it will be noticed that the absorption curve (Fig. 2) is similar to that of the α -isomeride both in form and position, although it is slightly less persistent,

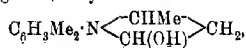
The condensation product of *m*-4-xylidine and acetaldehyde (α -form, m. p. 103–104°), $C_6H_3Me_2 \cdot NH \cdot CHMe \cdot CH_2 \cdot CHO$, was examined, and on comparing the curve (Fig. 3) with that of *m*-4-xylidine, it is noticeable that only one band is visible, the persistency of which is greater than that of the latter substance, and also greater than that of the corresponding compound obtained from *p*-toluidine. The band on the more refrangible side has

FIG. 3.



disappeared, exactly similar to the effect in the corresponding substance obtained from *p*-toluidine.

The β -compound (m. p. 127–128°), the constitutional formula of which, it is suggested, may be:



was examined, and the absorption curve (Fig. 3) is not unlike that of the α -compound, although it is not quite so persistent. There is therefore precisely the same kind of difference between these two substances as between the two corresponding substances obtained from *p*-toluidine.

It has been noticed by Hartley (*loc. cit.*), Baker and Baly (*Trans.*, 1907, 91, 1122), and Purvis (*Proc. Camb. Phil. Soc.*, 1908, 14, 436) that the effect of adding hydrochloric acid to the bases, pyridine, lutidine, and trimethylpyridine respectively was to produce a marked increase in the persistence of the absorption curves. The author has also shown (*Proc. Camb. Phil. Soc.*, 1908, 14, 568) that in tetrachloro-2-aminopyridine and tetrachloro-4-aminopyridine the absorption curves differ widely in their positions and persistencies, the orientation of the amino-group determining the nature and extent of the absorption; and, further, that the substitution of atoms forming part of a side-chain does not exert the same marked influence on the absorption of light as when the substitution takes place in the nucleus (*Trans.*, 1909, 95, 294).

In order to test how far the vibrations of the aromatic ring of the compounds of the present investigation are affected when the nitrogen atom is part of a side-chain, the absorption curve was studied when hydrochloric acid was added to the α -compound (m. p. 103–104°) obtained from *m*-4-xylydine. The results show (Fig. 3) that the form and persistency of the curve are not different from those of the latter compound. There is only a greater shift of the band towards the red end, caused by the weighting of the molecule by the acid. They confirm the view that the position and linking of the nitrogen atom in the ring or the side-chain is of considerable importance in determining the absorption of light.

Further, it will be noticed that in the bimolecular ethyldiene-xylydine the linking of the nitrogen atom of the two xylydine groups is different. On one side it is linked with two atoms of carbon and an atom of hydrogen; and on the other side it is linked with two atoms of carbon. In the latter case the linking of the nitrogen atom with a carbon atom of the aliphatic residue is a double one. The effect has been to reduce the absorption, and therefore the persistencies of the bands, although the general form of the curve has been retained.

The effect of the nitrogen linking in the α -compound obtained from *p*-toluidine has been to obliterate the more refrangible band, whilst the less refrangible one remains very similar to that of the parent substance both in form and persistency. The curve obtained

from the β -compound is also very similar, the only difference being that it is not so persistent. This difference probably indicates some alteration in the linking of the nitrogen atom, which may be in the direction of the suggested formula.

As regards the α - and β -compounds obtained from *m*-4-xyldine, which correspond with the α - and β -compounds obtained from *p*-toluidine, similar remarks apply, for the persistence of the curve of the β -compound is not so marked as that of the α -compound. The phenomena observed in the two series of compounds are precisely similar in this respect; and the linking of the nitrogen atom appears to be exactly the same.

It is not clear, however, how far these results assist the suggested formulæ of the β -compounds. We might have expected a somewhat different form of curve in compounds containing two rings of such different types. At the same time, there can be little doubt that the nitrogen atom is a determining factor in the absorption, and the suggestion that it is linked to three separate carbon atoms in these compounds, whereas in the isomerides it is linked to two carbon atoms, derives some support from the different persistencies of the bands. In such linkings the tendency would be to influence the vibrations so that less light would be absorbed, and it would be manifested in a decreased persistence of the absorption band. It is also conceivable that the vibrations of the aromatic ring are more fundamentally influenced by the combination with the nitrogen atom than are those of the aliphatic ring; or, in other words, if the aliphatic parts of the compounds are considered as displacing the hydrogen atoms of the amino-groups, the small differences shown by the curves may be explained by the previous observations that there is less influence on the vibrations of the nucleus in such a case than when the displacement takes place in the nucleus itself (Trans., 1909, 95, 294).

General Results.

The general results of the investigation show:

1. That the absorption curves of *p*-toluidine and *m*-4-xyldine are very similar. The chief differences are the slightly decreased persistence of the bands of *m*-4-xyldine, and the shifting of the bands of the heavier molecule towards the red end of the spectrum.
2. That the combination of two *m*-4-xyldine residues through acetaldehyde produces a greatly decreased persistence of the two bands and also a greater shift towards the red end.
3. That the isomeric substances obtained by the union of *p*-toluidine or of *m*-4-xyldine with acetaldehyde produce a disappearance of the more refrangible band found in the aromatic

compounds; and that the various substances show differences in the persistence of the remaining band, the origin of which may be explained from a consideration of differences in the nitrogen linking.

That the addition of hydrochloric acid to these derived compounds has no effect on the form and persistence of the absorption band, thereby indicating that the vibrations of the nucleus are not influenced by an alteration in the valency of the nitrogen of the side-chain.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

JOURNAL
OF
THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

Electro-syntheses. IV. SIMA M. LOSANITSCH (*Ber.*, 1909, **42**, 4394—4400. Compare Abstr., 1908, i, 2, 846, 866; ii, 32).—The substances investigated were submitted to the action of the silent electric discharge.

*iso*Pentane absorbs oxygen from the air, and is condensed to a mixture of higher saturated and unsaturated products, in which the latter predominate. *n*-Hexane is more slowly acted on; in this case the saturated products predominate.

Ethyl ether breaks down into formaldehyde, methane, and ethylene. The condensation products C_4H_8O and $C_8H_{14}O_2$ are formed, also ethylal, derived from formaldehyde and ether.

Acetaldehyde is decomposed to the extent of 80%, and condensed to 20% only. The decomposition products are mainly carbon monoxide and methane. The condensation products are polymerides of acetaldehyde and formaldehyde with aldehydic characteristics.

Formic and acetic acids are decomposed. Ethyl acetate gives hydrogen, methane, and carbon monoxide. The condensation products are $C_4H_8O_2$, corresponding with a bimolecular acetaldehyde, $C_8H_{16}O_4$, a combination of formaldehyde and ethyl acetate, and $(C_2H_5O)_n$, a higher polymeride of acetaldehyde. Chloroform yields an oil, $C_6H_5Cl_{12}$, and hexachloroethane.

Ethylene yields a volatile product, $C_{16}H_{20}O$, and a non-volatile product, $C_{26}H_{44}O_2$.

VOL. XXVIII. i.

Benzene gives a volatile compound, $(C_6H_6)_n$, and a non-volatile compound, $C_{24}H_{20}$.

Benzene and hydrogen form a colourless, oily, volatile liquid, $C_{12}H_{14}$, and a non-volatile, red, thick, clear substance, $C_{28}H_{34}$. E. F. A.

Formation of Naphthenes in Mineral Oil. I. CARL ENGLER (*Ber.*, 1909, 42, 4610—4613).—It is shown conclusively by the author, in conjunction with Routala (compare following abstracts), that olefines, which are formed by the distillation of fats under pressure, when heated under pressure at about 200° readily yield naphthenes and substances closely resembling mineral lubricating oils; consequently, the assumption that the naphthenes in mineral oils owe their origin to the action of a catalyst on olefines is unnecessary (compare Aschan, *Abstr.*, 1902, i, 749). W. H. G.

Formation of Naphthenes. II. Action of Aluminium Chloride on Amylene at Low and Moderately High Temperatures. CARL ENGLER and O. ROUTALA (*Ber.*, 1909, 42, 4613—4620).—A detailed account of the behaviour of various samples of amylene when treated with aluminium chloride at the ordinary temperature and at about 130° . Generally speaking, the results obtained are in good agreement with those recorded by Aschan (*Abstr.*, 1902, i, 749); thus, the more volatile products are composed mainly of paraffins, such as pentane, isopentane, hexane, β -dimethylbutane, γ -methylpentane, heptane, octane, decane, etc., whilst traces of naphthenes are present only in the fractions with high boiling points. W. H. G.

Naphthene Formation. III. Products Formed by Heating Amylene and Hexylene Under Pressure. CARL ENGLER and O. ROUTALA (*Ber.*, 1909, 42, 4620—4631).—When commercial amylene (β -methyl- Δ^2 -butylene) is heated under pressure at 320 – 325° for thirty-two days, it yields a gas (about 10 litres from 350 grams) and a liquid with a bluish-green fluorescence. The gas is composed of saturated hydrocarbons, paraffins, and polymethylenes, 91.1%; unsaturated hydrocarbons, 1.5%, and hydrogen, 7.4%. The liquid when fractionally distilled yields various paraffins, such as pentane, isopentane, hexane, heptane, and octane, whilst the higher boiling fractions (b. p. 130 – 250°) consist almost solely of naphthenes identical with, or very similar to, those which have been isolated by Markownikoff and Oglobin from Caucasian petroleum; for example, fractions were obtained having the composition and physical properties of nononaphthene, isodecanaphthene, β -decanaphthene, hendecanaphthene, tetradececanaphthene, and pentadecanaphthene; in addition, α -decanaphthene was isolated and identified as the nitro-derivative. The fractions with high b. p.'s closely resemble the mineral lubricating oils.

Δ^2 -Hexylene (methylpropylethylene), when heated under pressure at 325° for about thirty days, yields a mixture of gaseous, saturated hydrocarbons, and an oil from which fractions were obtained similar to those derived from amylene. W. H. G.

Chloroethylenes. KARL A. HOFMANN and HEINZ KIRMREUTHER (*Ber.*, 1909, 42, 4484-4485).—Whilst ethylene, its homologues and analogues combine rapidly with mercury salts, especially in presence of sodium acetate, di-, tri-, and tetra-chloroethylenes undergo no change under these conditions. With alkaline mercuric cyanide solutions, these haloid derivatives form salt-like, substituted compounds, the ethylene linking remaining intact (compare Abstr., 1908, i, 145); further, they are gradually reduced by platinum chloride, with which ethylene itself combines.

Iodine does not yield additive products with di-, tri-, or tetra-chloroethylene in the dark; with the trichloro-compound a slow action occurs in daylight, but the change is more complicated than simple addition.

The addition of bromine to these haloid derivatives in carbon tetrachloride solution in the dark takes place with measurable velocity (compare Plotnikoff, Abstr., 1906, ii, 12; Herz and Mylius, Abstr., 1907, i, 55; Bauer and Moser, Abstr., 1907, i, 307). With dichloroethylene the value of K calculated for a reaction of the second order is constant ($1.18-1.52.10^{-4}$). With tetrachloroethylene the value of K increases to an approximately constant magnitude, the auto-acceleration of the reaction being due to the catalytic action of an oxidation product, such as carbonyl chloride, the odour of which is observable.

In the case of trichloroethylene the reaction is very complex and irregular. The velocity, which initially is greater than with dichloroethylene, diminishes from $K = 4.06 \times 10^{-4}$ to 0.58×10^{-4} afterwards increasing to the value 2.57×10^{-4} . Here, also, the odour of carbonyl chloride is noticed, and either this compound or an analogous oxidation product doubtless exerts a considerable catalytic influence on the reaction.

T. H. P.

Esters of Perchloric Acid. KARL A. HOFMANN, [GRAF] ARMIN ZEDTWITZ, and H. WAGNER (*Ber.*, 1909, 42, 4390-4394. Compare Abstr., 1909, ii, 568).—The attempt was made to prepare alkyl-esters of perchloric acid by the interaction of nitrosyl perchlorate with alcohols. These perchlorates are formed, but even when very small quantities of substance are used and every precaution is adopted, they are of too explosive a nature to be isolated. The experiments were accordingly restricted to the preparation of esters of ethylene glycol and chlorohydrin, formed by the interaction of ethylene oxide and of epichlorohydrin with perchloric acid, D 1.72, containing sixty-three parts by weight of HClO_4 .

Chloroperchloratohydrin, $\text{ClO}_4 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \text{Cl}$, is a colourless, heavy oil. It burns like gun-cotton, explodes when struck more easily than nitroglycerin, but is easily hydrolysed by water and slowly decomposes in moist air. This excludes any practical application as an explosive.

The corresponding **chloronitratohydrin** does not explode, and is hardly hydrolysed at $+17^\circ$ under conditions which cause hydrolysis of more than half of the perchlorate.

Diethylene glycol monoperchlorate, $\text{ClO}_4 \cdot \text{C}_2\text{H}_4 \cdot \text{O} \cdot \text{C}_2\text{H}_4 \cdot \text{OH}$, is a colour-

less oil, which explodes violently when heated and burns like gun-cotton. It is slightly more stable towards moisture than the chloroperchlorato-hydrin, but slowly decomposes when exposed to the atmosphere.

E. F. A.

Sodium Alkyl Carbonates. ANTOINE P. N. FRANCHIMONT (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 303—304).—Sodium methyl and ethyl carbonates have been obtained by the action of dry carbon dioxide on the dry sodium alkyl oxide free from alcohol. Both substances are decomposed by water, but not by acetone, or yet when heated to about 180°. Whilst sodium phenyl carbonate is decomposed by acetone, it is shown that the rate of decomposition is greatly reduced if the acetone is dried over phosphoric oxide. H. M. D.

Kephalin. JAKOB PARNASS (*Biochem. Zeitsch.*, 1909, 22, 411—432).—Kephalin was prepared by extracting the hardened and dried brain with light petroleum. It was separated from the cholesterol and phosphatides by precipitation from this solution by alcohol. From the precipitate thus obtained it was extracted by a small quantity of very cold ether, and thus separated from the cerebrosides. The ratio of P : N in the carefully prepared product is 1:1. It readily undergoes hydrolysis with water, acids, and bases. On heating at 120° for twelve hours with barium hydroxide solution, it yields stearic acid, bases, and a barium salt, $C_{27}H_{53}O_{10}PBa_2$, the acid of which is obtained in a yield of about 50% of the kephalin hydrolysed.

On further hydrolysis with alkali, this phosphorus-containing tetrabasic acid yields "kephalinic" or "kephalinolic" acid in a yield equivalent to 18% of the kephalin. This was obtained pure in the form of the methyl ester, $C_{19}H_{34}O_2$, which, on treatment with hydrogen, is converted into methyl stearate, m. p. 37°, from which stearic acid, m. p. 69°, was obtained on hydrolysis. The kephalinic acid ester also takes up 1 molecule of oxygen on treatment with air. The free acid obtained from the ester by hydrolysis solidifies on cooling to -8°, but melts on warming to -4°. It boils at 205° in a vacuum, yielding apparently a mixture of free acid and the isomeric lactone. The barium salt, $(C_{18}H_{31}O_2)_2Ba$, is crystalline. The acid can be directly reduced by hydrogen in the presence of palladium to stearic acid. The sodium salt is soluble in ether. The author brings forward reasons for believing that kephalin is constituted differently from the lecithins.

S. B. S.

α -Bromopropionic Acid. LUDWIG RAMBERG (*Annalen*, 1909, 370, 234—239).—I. *1- α -Bromopropionic Acid*.—This acid has been carefully purified by repeated crystallisation and separation of the crystals from the liquid acid by means of a centrifuge; it has m. p. -0.3° to -0.5° (in a sealed capillary tube), D_4^{20} 1.700, D_4^{15} 1.692, $[\alpha]_D^{20}$ -29.0°, $[\alpha]_D^{25}$ -28.5° (compare *Abstr.*, 1906, i, 923). The acid racemises very slowly, the value of $[\alpha]_D^{20}$ changing from -27.0° in May, 1906, to -24.3° in July, 1909.

II. *Inactive α -Hydroxypropionic Acid*.—A metastable modification of this acid has been obtained by rapidly cooling the liquid acid to -30° ; it has m. p. -3.9° (corr.), and is very stable in the absence of the stable variety, but by inoculation changes spontaneously into this acid.⁴ The stable form has m. p. 25.7° (corr.), D₂₀ 1.700 (compare Weinig, Abstr., 1895, i, 16), and is undoubtedly the true racemic form of the acid.
W. H. G.

Melting and Solidifying Points of Fatty Substances.

I. *Binary Mixtures of Stearic, Palmitic, and Oleic Acids*. EMILIO CARLINFANTI and MARIO LEVI-MALVANO (*Gazzetta*, 1909, 39, ii, 353—375).—The authors discuss the various methods which have been suggested for the determination of the m. p. of fats, and give the results of their investigations on the solidification curves for the systems palmitic-stearic, palmitic-oleic, and stearic-oleic acids.

The solidification diagram for palmitic-stearic acid consists of two curves, the one for the system having for components stearic acid and the additive compound, $C_{16}H_{32}O_2, C_{18}H_{36}O_2$, and the other for the system comprising the additive compound and palmitic acid. The first of these curves, which meets the other at 56° , the crystallisation temperature of the additive compound, is of Roozeboom's type I, and shows neither a maximum nor a minimum, the solidifying point of stearic acid being lowered continuously by addition of the additive compound. The second curve is a combination of Roozeboom's types II and III, and exhibits a maximum at 56.25° and a minimum at 54.75° , neither of these temperatures corresponding with a simple compound of the two components. The additive compound hence forms with palmitic acid three different series of solid solutions.

The diagram for mixtures of stearic and oleic acids is of Roozeboom's type I, the m. p. of stearic acid being depressed at first slowly and afterwards rapidly as the addition of oleic acid is continued. These acids hence form a continuous series of solid solutions (compare Garelli and Montanari, Abstr., 1895, ii, 205). The mixture containing 5% of stearic acid begins to crystallise at 12.4° , after a superfusion of 0.2° , the temperature falling gradually to 7.8° , where a sudden jump to the solidification point of oleic acid takes place, followed by a very slow fall of temperature. This behaviour is explained by the separation at 12.4° of a solid solution, which is richer in stearic acid than the liquid, and does not enter into equilibrium with the liquid, that is, does not absorb oleic acid as the temperature falls. Gottlieb (*Annalen*, 1846, 57, 37) gave for oleic acid the m. p. 14° and the solidifying point 4° ; for their oleic acid, which gave an iodine number of 90.5 instead of the theoretical 90, the authors found the solidifying point 9° with 2.5° superfusion.

The system comprising palmitic and oleic acids exhibits behaviour similar to that of stearic and oleic acids.

The additive compound formed by palmitic and stearic acids probably represents the original margaric acid, the more recent daturic acid, and, possibly, the synthetic margaric acid assumed to exist at the present day.
T. H. P.

Melting and Solidifying Points of Fatty Substances. II. Ternary Mixtures of Palmitic, Stearic, and Oleic Acids. EMILIO CARLINFANTI and MARIO LEVI-MALVANO (*Gazzetta*, 1909, 39, ii, 375—385. Compare preceding abstract).—In order to obtain data for the determination of the proportions of palmitic, stearic, and oleic acids in a mixture of the three, the authors have investigated the solidifying points of fifty mixtures of the three acids.

With each mixture, the temperature falls regularly while the mixture remains liquid, rises 1—1.5° when crystallisation commences, then again falls slowly until crystallisation is complete, and subsequently more rapidly. In no case is an arrest of the temperature observed during the fall, so that the solid formed by the crystallisation of any one mixture of the acids is formed of a single phase, composed of solid solutions of the three acids, the miscibility of these in the solid state being complete. The results are given in the form of an equilateral triangle diagram. Each temperature of solidification is common to a series of mixtures, both of the three acids and of two of them, and, in order to determine whether a mixture under examination consists of two or three acids, and to ascertain the proportions of each, it is necessary either to estimate the stearic acid by Hehner and Mitchell's method, or to determine the iodine number. It is found that the iodine number corresponds very closely with the proportion of oleic acid in the mixture. The iodine numbers and the temperatures at which crystallisation commences are given for a number of mixtures of fatty acids derived from natural fats and oils.

T. H. P.

Hydrolysis of Fats and Oils. RUDOLF WECSCHIEDER (*Chem. Zeit.*, 1909, 33, 1220).—Some remarks on Kellner's paper (*Abstr.*, 1909, i, 759).

Kellner's observations are in harmony with the theory of a gradual saponification.

L. DE K.

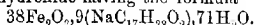
Detergent Action of Soap Solutions. Part II. WALTHER SPRING (*Rec. trav. chim.*, 1909, 28, 424—443).—In the previous paper of this series (*Abstr.*, 1909, i, 628) the detergent action of soap solutions for lampblack was considered, and in the present paper the investigation is extended to ferric compounds, and more especially "red ochre." The conclusions as to the general mode of action of soap, already indicated, are confirmed.

The red ochre employed had the composition represented by the formula $7\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. As in the case of lampblack, so with ochre (*loc. cit.*), an optimum concentration of soap solution exists, from which the rate of deposition of the ochre is a minimum. This concentration is about 0.5%. The colloidal compound formed between soap and ochre is slightly soluble in water, so that all the solutions used retained a red colour even after the deposition of the ochre. Evidence as to the formation of this colloidal compound was obtained by analysis of soap solutions in water or methyl alcohol, in which ochre had been suspended. The ashes from these were less in amount than those from the original soap solutions, showing that a portion of

the soap had been carried out by the ochre. It appears, therefore, that, as with lampblack, the soap is decomposed into a basic portion and an acid portion, the former being carried down by the ochre. The deposition of ochre from suspension in water is accelerated by alkalis or acids so long as more than 0.078% of alkali or more than 0.0001% of acid is present.

Water containing ochre in suspension may be filtered clear eventually by passing it many times through filter paper, but the ochre deposited in such filter paper is again carried through by soap solution. The amount of ochre thus carried through by soap solution does not increase with the concentration of the latter until this falls below 0.25%.

Soap solutions tend to flocculate colloidal solutions of ferric hydroxide, and a minimum molecular concentration (1 mol. soap to 2.16 mols. of ferric oxide) exists, at which turbidity but no precipitation occurs, and a maximum concentration (1 mol. soap to 3.47 mols. of ferric oxide), at and beyond which complete flocculation of the ferric compound takes place. The precipitate formed is yellow in colour, but on drying becomes chocolate-brown, and is a colloidal compound of soap and ferric hydroxide having the formula



It does not adhere to glass, paper, or skin, and is quite different in properties from "ferric soap" prepared in the usual way by double decomposition. The results indicate that the detergent property of soap for ferric hydroxide is due to the formation of a colloidal compound of the two substances, which no longer has the property of adhering to fabrics or tissues.

T. A. H.

Hydroxyaliphatic Acids from the Products of the Interaction of Hypochlorous Acid or Chlorine and the Glycerides of Aliphatic Acids of Animal or Vegetable Origin. GEORGES INERT and CONSORTIUM FOR ELEKTROCHEMISCHE INDUSTRIE (D.R.P. 214154. Compare Abstr., 1909, i, 875).—Instead of preparing the dihydroxyaliphatic acids from the product of the action of chlorine or hypochlorous acid on the fatty acids themselves, their glycerides may be employed, and the hydrolysis of the dichloro- or chlorohydroxy-glyceride can be effected at the same time as the replacement of chlorine by hydroxyl.

The glyceride of chlorohydroxystearic acid, obtained by the action of hypochlorous acid on olive oil, was heated with a 7% solution of sodium carbonate at 150°, and the dihydroxystearic acid precipitated with sulphuric acid.

The glyceride of dichlorostearic acid, produced by the action of chlorine on olive oil, is hydrolysed in the same way. F. M. G. M.

Stereochemistry of the Glutaconic Acid Group. FRANZ FEIST (*Annalen*, 1909, 370, 41—60. Compare Perkin, *Trans.*, 1897, 71, 1182; 1902, 81, 246; 1903, 83, 8, 771).—A theoretical paper devoted to a discussion of the stereoisomerism of alkyl derivatives of glutaconic acid and of the observations recorded in the following abstracts and p. i, 39.

It is found that α -methylglutaconic acid in analogy to β -methylglutaconic acid (compare Feist, Abstr., 1906, i, 334) exists in two stereoisomeric modifications, thus providing another case against the view advanced by Thorpe (Trans., 1905, 87, 1669). Attempts to prepare two isomeric β -phenylglutaconic acids have been unsuccessful.

Many alkyl derivatives of glutaconic acid have been isolated in one form only, and in cases where the anhydride has been prepared, as, for example, the α -dimethyl, β -methyl- α -ethyl, and $\alpha\beta\gamma$ -trimethyl derivatives, these compounds have been regarded as the *cis*-modifications. The great stability of these compounds and the impossibility of converting them into the more stable *trans*-isomerides made it appear probable that, notwithstanding the close relationship existing between the acid and its anhydride, the acid might be the *trans*-form produced by the spontaneous transformation of the *cis*-isomeride at the moment of its production from the anhydride. Attempts were made, therefore, to prevent the transformation of the *cis*-compound into the *trans*-form by acting on the anhydride with alkali in the presence of an anti-catalyst, and with success; for example, the anhydride of α -methylglutaconic acid when treated with alkali in the presence of casein and subsequently with silver nitrate yields a silver salt, which, when decomposed by hydrogen sulphide, gives the *cis*-acid, m. p. 118° ; in the absence of casein, the *trans*-acid, m. p. 145 – 146° , containing traces of the *cis*-isomeride, is obtained.

The effect on the stability of the stereo-isomerides produced by the replacement of the various hydrogen atoms of glutaconic acid by alkyl groups may be summarised as follows: (1) Replacement of the two α -hydrogen atoms renders the isomerides very stable; they cannot be converted one into the other; if only one atom is substituted, then the isomerides may with difficulty be transformed one into the other. The effect of alkyl groups in the α -position is neutralised to some extent by substitution of a β - or γ -hydrogen atom; thus, *cis*- $\alpha\gamma$ -trimethylglutaconic acid passes quite readily into the *trans*-acid. (2) The compounds obtained by replacing a β - or γ -hydrogen atom by an alkyl group, even if one of the α -hydrogen atoms is likewise replaced by an alkyl group, have been obtained only in the stable *trans*-form, with the exception of β -methylglutaconic acid (compare Perkin, Trans., 1902, 81, 246; Thorpe, Trans., 1905, 87, 1669; Perkin and Thorpe, Trans., 1898, 71, 1182).

The readiness with which the glutaconic acids yield anhydrides depends largely on the position of the alkyl groups; in agreement with the results of Victor Meyer and of Anwers, the tendency to form an anhydride is increased by the accumulation of alkyl groups, but it is found that substitution of the β -hydrogen atom leads more particularly to the ready formation of anhydrides; thus, $\alpha\beta\gamma$ -trimethylglutaconic acid, $\alpha\beta$ -dimethylglutaconic acid, β -phenylglutaconic acid, and β -methylglutaconic acid yield anhydrides when fused, whereas $\alpha\gamma$ -dimethylglutaconic acid and α -methylglutaconic acid do not yield anhydrides when treated similarly.

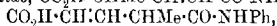
The stability of the anhydrides towards the addition of water, likewise the ability of the various glutaconic acids to form additive

products, depends largely on the position of the alkyl group, but rules of general applicability cannot be given. W. H. G.

Stereoisomeric α -Methylglutaconic Acids. FRANZ FEIST and G. POMME (*Annalen*, 1909, 370, 61—72. Compare preceding abstract).—Ethyl sodiodicarboxylglutaconate when treated with an alcoholic solution of methyl sulphate yields ethyl dicarboxymethylglutaconate, which, when hydrolysed with aqueous alkali or hydrochloric acid, yields a mixture of two isomeric α -methylglutaconic acids, melting at 145—146° and 118° respectively. The acid m. p. 145—146°, first described by Conrad and Guthzeit, is shown to be the *trans*-modification, since α -methylglutaconic anhydride absorbs water from the air, yielding the acid, m. p. 118°, and when treated with alkali in the presence of casein yields the same acid, m. p. 118°; the crystalline calcium ($2\frac{1}{2}\text{H}_2\text{O}$) and barium ($2\text{H}_2\text{O}$) salts were analysed; the acid changes partly into the *cis*-isomeride when treated with dilute hydrochloric acid or aqueous sodium hydroxide.

cis- α -Methylglutaconic acid, $\text{C}_6\text{H}_8\text{O}_4$, m. p. 118°, does not alter when fused, but is partly converted into the *trans*-isomeride by hot dilute hydrochloric acid; the barium ($2\text{H}_2\text{O}$) and calcium ($4\text{H}_2\text{O}$) salts were analysed.

α -Methylglutaconic anhydride, $\text{C}_6\text{H}_6\text{O}_3$, cannot be prepared by the action of acetyl chloride or thionyl chloride on the acid, but is obtained by treating the acid with phosphorus pentachloride; it crystallises in long needles, m. p. 85°, and when warmed with aniline yields the *semianilide*, $\text{CO}_2\text{H}\cdot\text{CHMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{NHPh}$ or



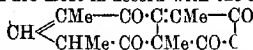
crystallising in white needles, m. p. 165°.

trans α -Methylglutaconic acid interacts (1) with aniline at 150°, yielding *α -methylglutaconanil*, $\text{CH}\begin{smallmatrix} \text{CHMe}\cdot\text{CO} \\ \text{CH}\text{---}\text{CO} \end{smallmatrix}\text{NPh}$, which crystallises in needles, m. p. 229°, and (2) with hydrobromic acid in glacial acetic acid, with the formation of *bromo- α -methylglutaconic acid*, $\text{C}_6\text{H}_7\text{O}_4\text{Br}$, crystallising in needles, m. p. 141°.

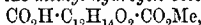
An attempt to prepare α -methylglutaconic acid by reducing ethyl methylacetonedicarboxylate, heating the product with acetic anhydride, and hydrolysing the ester so formed, led to the isolation of a *substance*, $\text{C}_{11}\text{H}_{14}\text{O}_8$, m. p. 141°. W. H. G.

$\alpha\gamma$ -Dimethylglutaconic Acids. FRANZ FEIST and R. REUTER (*Annalen*, 1909, 370, 82—92. Compare preceding abstracts; Reformatzky, Abstr., 1899, i, 481; Blaise, Abstr., 1903, i, 400, 548).—The object of this investigation was to prepare a second $\alpha\gamma$ -dimethylglutaconic acid by making use of casein as an anti-catalyst; this could not be done, however, owing to the impossibility of preparing a normal anhydride of the acid. $\alpha\gamma$ -Dimethylglutaconic acid does not pass into the anhydride when fused or when heated with acetyl chloride, thionyl chloride, or concentrated sulphuric acid. When warmed with phosphorus pentachloride it yields small quantities of a

substance, $\text{CH} \begin{smallmatrix} \text{C}_{12}\text{H}_{10}\text{O}_6 \\ \text{CO} \cdot \text{CO} \cdot \text{CO} \cdot \text{CO} \cdot \text{CO} \cdot \text{CO} \end{smallmatrix} \text{OH}$ (9), crystallising in small needles, m. p. 82–83°, and relatively large quantities of a substance, the properties of which are most in accord with the formula



The latter substance forms white crystals, m. p. 207–208°, and undergoes the following changes: (1) when boiled with water it yields the dibasic acid, $\text{C}_{14}\text{H}_{10}\text{O}_6$, m. p. 176–176.5° (decomp.); (2) when treated with aniline, it yields the *semianilide*, $\text{CO}_2\text{H} \cdot \text{C}_{12}\text{H}_{10}\text{O}_2 \cdot \text{CO} \cdot \text{NHPh}$, m. p. 247–248°, and a substance, m. p. 151°, obtained as a white powder; (3) it is converted by a solution of sodium methoxide in methyl alcohol into the *methyl hydrogen ester*,



a white, crystalline substance, m. p. 183–183.5°, and a crystalline substance, $\text{C}_{15}\text{H}_{20}\text{O}_4$, m. p. 142–143°; (4) it combines with bromine, yielding a *dibromo-derivative*, $\text{C}_{14}\text{H}_{14}\text{O}_5\text{Br}_2$, m. p. 163°. W. H. G.

Derivatives of Propylsuccinic Acid. RENÉ LOCQUIN (*Bull. Soc. chim.*, 1909, [iv], 5, 1071–1074).—Propylsuccinic acid (m. p. 91–92°) was prepared by Waltz's process (Abstr., 1882, 948), and converted into the anhydride, b. p. 145–150°/13 mm., by heating it, complete transformation being secured by boiling the product with acetic anhydride. The following new derivatives suitable for the identification of the acid are described.

With aniline the anhydride yields the *monoanilide*, m. p. 123–126°, which crystallises from benzene on adding alcohol, and on heating at 180–200° during fifteen minutes passes into the *anil*, m. p. 83°, which crystallises from a mixture of alcohol and light petroleum.

Ethyl propylsuccinate has b. p. 132–134°/25 mm. The methyl ester, b. p. 107°/11 mm. or 112°/15 mm., on treatment with ammonia yields the *diamide*, m. p. 234–235°, which crystallises in colourless needles from alcohol containing acetic acid. With hydrazine hydrate the methyl ester yields the *dihydrazide*, m. p. 176°, which separates from alcohol as a white powder, and condenses with benzaldehyde to give a *dibenzylidene* derivative, m. p. 226°, a white powder, which is difficult to purify by reason of its insolubility in organic solvents.

T. A. H.

Cholic Acid. I. MARTIN SCHENCK (*Zeitsch. physiol. Chem.*, 1909, 63, 308–312).—When an alkaline solution of dehydrocholic acid (Hammarsten, Abstr., 1881, 624; Mylius, *ibid.*, 1886, 952; 1887, 983) is reduced electrolytically, using lead terminals and a porous cell, the chief product is *reductodehydrocholic acid*, $\text{C}_{24}\text{H}_{42}\text{O}_6$, a compound intermediate between cholic and dehydrocholic acids. The acid crystallises from benzene in minute, colourless needles, m. p. 188°, and yields a *dioxime*, $\text{C}_{24}\text{H}_{38}\text{O}_5(\text{NOH})_2$, which crystallises from alcohol in slender needles decomposing at 254–256°. J. J. S.

American Colophony. PAUL LEVY (*Ber.*, 1909, 42, 4305—4308).—When sodium abietate from American colophony is oxidised with a 2% solution of potassium permanganate at the ordinary temperature, the products are tetrahydroxyabietic acid, propionic acid, isobutyric acid, and resins. The tetrahydroxy-derivative, $C_{20}H_{34}O_6$, is separated from the resins by treatment with acetone, when it forms a colourless powder, which crystallises in well-developed crystals, m. p. 246—247° (decomp.). The silver salt, $C_{20}H_{34}O_6Ag \cdot 2.5H_2O$, and barium salt, $C_{40}H_{68}O_{12}Ba \cdot 4H_2O$, are described.

The tetrahydroxy-acid is probably identical with Fabron's tetrahydroxysylvic acid (*Abstr.*, 1901, i, 166), and the formation of the acid is regarded as supporting the author's view that abietic acid contains two ethylene linkings.

J. J. S.

Catalytic Preparation of Unsymmetrical Aliphatic Ketones. JEAN B. SENDRENS (*Compt. rend.*, 1909, 149, 995—997. Compare *Abstr.*, 1909, i, 286, 627).—The method for the preparation of symmetrical ketones already described has now been extended to the production of mixed ketones; thus methyl ethyl ketone is obtained by passing a mixture of the vapours of acetic and propionic acids over thorium dioxide at 400—430°. Acetophenone and acetone are obtained when acetic acid (3 mols.) and benzoic acid (1 mol.) are employed. The separation of the unsymmetrical ketones from the accompanying smaller quantities of symmetrical products is easily effected by fractionation.

W. O. W.

Synthesis of Ketones by means of Organo-magnesium Compounds. [JULIUS SALKIND and (Madame) T. BENURISCHWILI (*Ber.*, 1909, 42, 4500—4502).—The diminution of the reactivity of the carboxyl group towards organo-magnesium compounds, produced by a second carboxyl group (compare Simonis and Arand, *Abstr.*, 1909, i, 932), probably accounts for the formation of esters of β -keto-acids by the action of magnesium on esters of α -bromo-acids (compare *Abstr.*, 1907, i, 22; Zeltner and Reformatsky, *Abstr.*, 1907, i, 23; Salkind and Baskoff, *J. Russ. Phys. Chem. Soc.*, 1908, 40, 327). In this case the magnesium compound, $MgBr \cdot CH_2 \cdot CO_2Et$, formed in the ordinary way, condenses immediately with its own carboxyl group, yielding a product of the formula: $MgBr \cdot CHR \cdot C(OEt)(OMgBr) \cdot CHR \cdot CO_2Et$, which gives a good yield of a substituted acetoacetic ester when decomposed by means of water. Tertiary hydroxy-acids are never obtained in this way, so that with them, addition of a second molecule of the Grignard compound does not occur.

The authors have investigated the action of Grignard's compounds on the sodium salts of carboxylic acids (compare Grignard, *Abstr.*, 1904, i, 213; Farbenfabriken vorm. Friedr. Bayer & Co., *Abstr.*, 1906, i, 660). When perfectly dry sodium acetate or propionate is added, with cooling and continual stirring, to the calculated proportion of the organo-magnesium compound, and the mixture decomposed after twenty-four hours by iced water, the ketone is obtained, the yield of crude product being 25—27%. Thus, with magnesium iso-

butyl bromide and sodium acetate, methyl isobutyl ketone is obtained; with magnesium isoamyl iodide and sodium acetate, methyl isoamyl ketone; with magnesium phenyl bromide and sodium acetate, acetophenone; and with magnesium ethyl bromide and sodium propionate, diethyl ketone.

T. H. P.

The Hexosephosphate Formed by Yeast-Juice from Hexose and a Phosphate. WILLIAM J. YOUNG (*Proc. Roy. Soc.*, 1909, B, 81, 528—545. Compare Abstr., 1905, ii, 109; 1906, i, 470; 1908, ii, 590; 1909, i, 863).—The compound formed during the accelerated fermentation of dextrose, lævulose, and mannose by yeast-juice in the presence of a soluble phosphate is a salt of an acid which probably has the formula $C_6H_{10}O_4(PO_4H_2)_2$, and may be isolated by precipitation of its lead salt. The free acid may be obtained in solution by decomposing this lead salt with hydrogen sulphide. The acid is very unstable, and readily decomposes on keeping, or on evaporating even at the ordinary temperature in a vacuum over sulphuric acid, with formation of a reducing substance and phosphoric acid. It reduces Fehling's solution, but no osazones or hydrazones have been obtained from it. No differences have been detected between the hexosephosphoric acids or their salts, whether derived from dextrose, lævulose, or mannose. The salts of lead, barium, silver, and cadmium have been prepared.

G. S. W.

Platinum. ALEXANDER GUTHRIE and FR. BAURIEDL (*Ber.*, 1909, 42, 4243—4249. Compare Abstr., 1903, ii, 488).—In connexion with the revision of the atomic weight of platinum, the authors have prepared a number of substituted ammonium salts of hydrogen platinibromide. A solution of hydrogen platinichloride was evaporated on the water-bath six times with concentrated hydrobromic acid. The residue was then treated several times in a similar manner with hydrobromic acid containing bromine, and the final residue dissolved in dilute hydrobromic acid. In this way a dark carmine-red solution was obtained, from which crystals of hydrogen platinibromide, $H_2PtBr_6 \cdot 9H_2O$, separated on evaporation over lime. By the addition of solutions of substituted ammonium bromides to this solution, the following platinibromides were precipitated in a pure condition.

Methylammonium platinibromide, $(NH_4Me)_2PtBr_6$: light brown to reddish-brown, six-sided, regular plates, which are still solid at 260°.

Dimethylammonium platinibromide, $(NH_2Me_2)_2PtBr_6$: slender, red, rhombic prisms, m. p. 232° (decomp.). *Trimethylammonium platinibromide*, $(NHMe_3)_2PtBr_6$: dark red octa- and hexa-hedra, m. p. 253—254° (decomp.). *Ethylammonium platinibromide*, $(NH_4Et)_2PtBr_6$: yellowish-red, six-sided, regular plates, which are still solid at 264°. *Diethylammonium platinibromide*, $(NH_2Et_2)_2PtBr_6$, monoclinic plates, m. p. 251—252° (decomp.). *Triethylammonium platinibromide*, $(NH(Et)_3)_2PtBr_6$: ruby-red crystals, probably monoclinic, m. p. 231—232°. *n-Propylammonium platinibromide*, $(NH_3Pr^s)_2PtBr_6$, red, monoclinic plates, m. p. 257—258° (decomp.). *iso-Propylammonium platinibromide*, $(NH_3Pr^i)_2PtBr_6$: yellowish-red, six-sided plates, m. p.

267°. *n*-Butylammonium platinibromide, $(C_4H_9 \cdot NH_2)_2PtBr_6$: yellowish-red, six-sided plates, m. p. 256°. *iso*Butylammonium platinibromide, $(C_4H_9 \cdot NH_2)_2PtBr_6$: ruby-red, monoclinic prisms, m. p. 266°. Ethylenediammonium platinibromide, $C_2H_4N_2PtBr_6$: red, six-sided prisms, which remain solid at 270°. Propylenediammonium platinibromide, $C_3H_7N_2PtBr_6$: dark red prisms, which are still solid at 270°.

T. S. P.

Preparation of Hydroxamic Acids from Hydroxylamine Salts of Organic Acids. LAUDER WILLIAM JONES and RALPH OESPER (*Amer. Chem. J.*, 1909, 42, 515—520).—When hydroxylamine formate (Sabeneff, Abstr., 1900, ii, 14), m. p. 76°, is left for several weeks at the ordinary temperature, or heated for a few minutes at its m. p., it is partly converted into formhydroxamic acid. If, however, the salt is heated above 80°, violent decomposition occurs. The reaction is reversible, and it is shown that formhydroxamic acid can be synthesised by treating hydroxylamine with dry carbon monoxide. When hydroxylamine acetate is heated at 90° in a sealed tube, acethydroxamic acid is produced in a yield of about 25—30%. Preliminary experiments have shown that hydroxylamine benzoate and anisate also yield the corresponding hydroxamic acids when heated slightly above their m. p.'s.

E. G.

Reaction between Hydrogen Sulphide and Cyanaminodithiocarbonates. ARTHUR ROSENHEIM (*Ber.*, 1909, 42, 4439—4440).—Polemical. A reply to Hantzsch (Abstr., 1909, i, 894; compare Rosenheim, Levy, and Grünbaum, *ibid.*, i, 776).

R. V. S.

Dithiourethanes. II. Preparation of Thioglycols from Bisdithiourethanes. JULIUS VON BRAUN (*Ber.*, 1909, 43, 4568—4574. Compare Abstr., 1902, i, 271).—The behaviour of dihalogen substituted aliphatic hydrocarbons towards dithiocarbamates has been studied to test the influence of the distance between the halogens on the introduction of the thiourethane complex. The reaction between $\omega\omega'$ -di-iodo-ethane, -propane, -butane, -pentane, -hexane, and -decane and a dithiocarbamate takes place readily and with equal velocity at both ends of the molecule, forming only bisdithiourethanes, $NR_2 \cdot CS \cdot S \cdot [CH_2]_x \cdot S \cdot CS \cdot NR_2$, and never iododithiourethanes, $NR_2 \cdot CS \cdot S \cdot [CH_2]_x \cdot I$.

The products are indifferent substances; the piperidine derivatives, $C_5NH_{10} \cdot CS \cdot S \cdot [CH_2]_x \cdot S \cdot CS \cdot C_5NH_{10}$, have been analysed. They crystallise remarkably well, and the melting point only slowly falls with an increase in the length of the chain. The *propane* derivative has m. p. 140°; *butane* derivative, m. p. 125°; *pentane* derivative, m. p. 103°; *hexane* derivative, m. p. 94°; *decane* derivative, m. p. 90°.

The di-iodo-compounds interact similarly with carbon disulphide and primary amines, but the dithiourethanes formed are more soluble, and were only obtained as viscid oils which decompose when warmed.

On mixing finely powdered ammonium dithiocarbamate with the di-iodo-compounds in alcoholic solution, a colourless precipitate

gradually forms; the time of formation of this does not seem to depend on the molecular weight of the iodide. The bisdithiourethanes formed were not obtained quite pure, and did not show sharp melting points. They softened from 100° to 150°. When warmed with potassium hydroxide, they are converted into the corresponding thioglycols.

Butylene αδ-dithiol, $\text{HS} \cdot [\text{CH}_2]_4 \cdot \text{SH}$, is a colourless oil, b. p. 105—106°/30 mm.; the *benzoyl* derivative forms long needles, m. p. 49°.

Hexylene αζ-dithiol, $\text{HS} \cdot [\text{CH}_2]_6 \cdot \text{SH}$, has b. p. 118—119°/15 mm.; the *benzoate* has m. p. 57°.

Decalene ακ-dithiol has b. p. 176°/16 mm., m. p. 20°; the *benzoate* has m. p. 55°. It is almost without odour. E. F. A.

Compounds from Guanylcarbamide and Diguanide. JULIUS SÖLL and ALBERT STUTZER (*Ber.*, 1909, 43, 4532—4541).—On evaporating dicyanodiamide with mineral acids, salts of guanylcarbamide are obtained, from which the free base has been prepared. To prepare dicyanodiamide, crude commercial cyanamide is stirred to a paste with water, boiled, and filtered hot; the dicyanodiamide crystallises from the filtrate. When evaporated with sulphuric acid, *guanylcarbamide hydrogen sulphate*, $\text{NH} \cdot \text{C}(\text{NH}_2) \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2 \cdot \text{H}_2\text{SO}_4$, is formed, which when decomposed with barium hydroxide gives guanylcarbamide. This crystallises from alcohol + $\text{C}_2\text{H}_5\text{O}$ in lustrous, glass-like prisms, which very rapidly take up carbon dioxide from the air. The alcohol evaporates in a desiccator. The free base has m. p. 105°; it evolves ammonia at 160°, or on boiling with water. The *picrate* crystallises in yellow plates, m. p. 265° to a clouded, yellow mass, decomp. 285°; it may be used to estimate guanylcarbamide quantitatively. The heat of combustion of guanylcarbamide nitrate is 327.4 Cal. Guanylcarbamide condenses readily in alcoholic solution, forming pyrimidine bases.

Guanylcarbamidesulphonic acid, $\text{C}_2\text{H}_5\text{ON}_4 \cdot \text{SO}_3\text{H}$, is obtained by heating guanylcarbamide sulphate with acetic anhydride; it crystallises in prisms, decomp. 220—230°; the *ammonium* salt forms short, thick prisms, m. p. 165—167°; the *barium* and *calcium* salts are similar. Acetic anhydride and sulphuric acid convert the sulphonic acid into acetylguanylcarbamide.

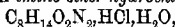
Acetylsulphuric acid acts on acetanilide to form acetylsulphanilic acid, crystallising in long needles from acetic acid (compare Schröter, *Abstr.*, 1906, i, 415).

Guanylcarbamide condenses with monochloroacetic acid on heating to guaninoacetic acid (*Ramsay*, *Abstr.*, 1909, i, 88). It forms a *picrate* crystallising in plates, m. p. 235—237°, differing from that described by *Ramsay*, m. p. 201° (*loc. cit.*). The new guaninoacetic acid is probably bimolecular; when boiled with hydrogen chloride, the hydrochloride of unimolecular guaninoacetic acid is formed, which gives the *picrate*, m. p. 202°. E. F. A.

Action of Hydrogen Chloride on Acetone Cyanohydrin. A. J. ULTÉE (*Rec. trav. chim.*, 1909, 28, 349—353. Compare *Pinner*, *Abstr.*, 1884, 1292).—When dry hydrogen chloride is passed into

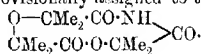
acetone cyanohydrin, cooled to 0° , two condensation products are formed.

The first of these is an *imino-ether hydrochloride*,



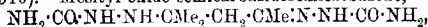
m. p. 231° (decomp.), and remains undissolved when the reaction product is mixed with rather less than its own volume of water. It is readily soluble in water, is precipitated therefrom by hydrochloric acid, and, on addition of alkalis, yields the *imino-ether*, which does not melt even at 280° , and on boiling with excess of alkali dissolves with evolution of ammonia, but, unlike most substances of this class, is not decomposed by water. The formula $\text{HO}\cdot\text{CMe}_2\cdot\text{C}(\text{NH})\cdot\text{O}\cdot\text{CMe}_2\cdot\text{CN}$ or $\text{HN}\cdot\text{C}\begin{smallmatrix} \diagup \text{O}\cdot\text{CMe}_2 \\ \diagdown \text{O} \end{smallmatrix} \text{C}\cdot\text{NH}$ is provisionally assigned to this substance.

The second product, $\text{C}_{12}\text{H}_{18}\text{O}_5\text{N}$, m. p. 193° , separates almost at once in colourless crystals from that part of the reaction mixture which is miscible with water. It is slightly soluble in water, readily so in chloroform, acetone, or alkalis, but is precipitated from solutions in alkalis by acids. When boiled with alkalis, it evolves ammonia, and on long boiling with hydrochloric acid forms *a-isobutyric acid*. The following formula is provisionally assigned to this product:



T. A. H.

Constitution and Behaviour of Semicarbazidesemicarbazones. HANS RUPE and SIDONIUS KESSLER (*Ber.*, 1909, **42**, 4503—4510).—Mesityl oxido semicarbazidesemicarbazone,

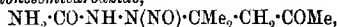


obtained in the form of the hydrochloride by the gradual action of semicarbazide hydrochloride on mesityl oxide, is stable in dilute aqueous alkalis, giving solutions which reduce ammoniacal silver nitrate and Fehling's solutions; the *hydrochloride*, $\text{C}_8\text{H}_{13}\text{O}_2\text{N}_6\text{Cl}$, forms microscopic, white needles, m. p. $211-212^{\circ}$ (decomp.).

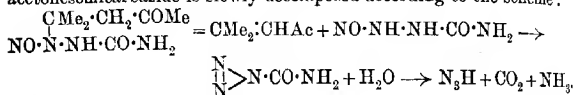
When a solution of the above semicarbazidesemicarbazone in dilute hydrochloric acid is treated with benzaldehyde, the semicarbazide residue united by a double linking to the carbon atom of the ketonic group is removed and benzaldehydesemicarbazone formed, together with diacetonesemicarbazide, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CMe}$, which can be separated as a nitroso-derivative. If the aqueous solution containing diacetonesemicarbazide hydrochloride is left for some time and then extracted with ether, the latter contains the compound obtained (1) by Scholtz (*Abstr.*, 1896, i, 343) by distilling mesityl oxido semicarbazone; (2) by Harries and Kaiser (*Abstr.*, 1899, i, 637) by the direct action of semicarbazide hydrochloride on mesityl oxide, and (3) by Rupe and Schlochoff (*Abstr.*, 1904, i, 144) by boiling mesityl oxido semicarbazidecarbazone with water. This compound, m. p. 131° , being formed from diacetonesemicarbazide, cannot be represented by the first of the two formulæ given by Harries and Kaiser (*loc. cit.*), although the evidence is insufficient to establish the accuracy of the second formula. In aqueous solution the compound reduces gold chloride in the cold and ammoniacal silver solution on

heating; by 10—15% sodium hydroxide solution it is only slowly and sparingly decomposed, with evolution of ammonia, and boiling with acids does not result in the removal of a $\cdot\text{CO}\cdot\text{NH}_2$ group. With nitrous acid, it yields mesityl oxide and carbamineazoimide (Thiele and Stange, Abstr., 1895, i, 252), which can arise only from a semicarbazone or from free semicarbazide, so that the ring-compound would appear to have been first resolved.

Nitrosodiacetonesemicarbazide,



prepared by the action of nitrous acid on diacetonesemicarbazide, or, together with carbamineazoimide, by the action of nitrous acid (2 mols.) on mesityl oxide semicarbazidesemicarbazone (1 mol.), forms white, rectangular plates, m. p. 145—146° (decomp.), gives Liebermann's reaction, is partly decomposed by water or mineral acids, forming azoimide, and when heated above its m. p. yields nitrogen, nitric oxide, carbon dioxide, ammonia, and azoimide. With semicarbazide (1 mol.) it gives *nitrosodiacetonesemicarbazidesemicarbazone*, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}(\text{NO})\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, which forms small, white needles, m. p. 158°. By alkali in the cold, nitrosodiacetonesemicarbazide is slowly decomposed according to the scheme:



When nitrosodiacetonesemicarbazide is dissolved in concentrated hydrochloric acid, acetic acid, 40% phosphoric acid, or acetic anhydride, and the solution subsequently diluted, and treated with semicarbazide hydrochloride and potassium acetate, a compound, $\text{C}_8\text{H}_{11}\text{O}_2\text{N}_3$, forming aggregates of slender needles, m. p. 172°, is obtained, which is decomposed by water or dilute sulphuric acid, giving azoimide, and by dilute hydrochloric acid, yielding benzaldehydesemicarbazone. T. H. P.

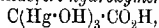
Metallic Derivatives of Chloro- and Bromo-acetylene. KARL A. HOFMANN and HEINZ KIRMREUTHER (*Ber.*, 1909, 42, 4232—4238. Compare Abstr., 1908, i, 145).—Mercury tribromoethylene, $\text{Hg}(\text{CBr}\cdot\text{CBr})_2$, crystallises in well-developed monoclinic prisms [$a : b : c = 1.4829 : 1 : 0.5637$; $\beta = 105^\circ 26'$].

Mercury chloroacetylide, $\text{Hg}(\text{C}\cdot\text{CCl})_2$, obtained by shaking δ -dichloroethylene with mercuric cyanide and aqueous potassium hydroxide solution, crystallises in thin, quadratic plates. The crystals exhibit strong double refraction, and decompose at 195°. When mixed with an ethereal solution of iodine and exposed to sunlight, the mercury compound yields *chlorotri-iodoethylene*, $\text{CClI}\cdot\text{ClI}_2$, which crystallises in long plates, m. p. 78—80°.

Mercury bromoacetylide, $\text{Hg}(\text{C}\cdot\text{CBr})_2$, can be prepared from dibromoethylene and an alkaline solution of mercuric cyanide, or by passing the gases, obtained by the action of alcoholic potassium hydroxide on tribromoethylene, into an alkaline solution of mercuric cyanide. It crystallises in thin, rectangular plates, which decompose at 153—155°, and detonate when rubbed on a porous plate. It is volatile

in steam, and is decomposed by boiling with dilute hydrochloric acid or potassium cyanide solution, yielding bromoacetylene. It readily forms an additive compound with mercuric bromide in the form of an amorphous powder. Pure chloro- and bromo-acetylene are readily prepared by warming the respective mercury compounds with potassium cyanide solution, care being taken that the air in the apparatus is replaced by hydrogen. When chloroacetylene is passed into ammoniacal silver nitrate solution, a white precipitate of $\text{AgO}:\text{CCl}$ is formed. This darkens rapidly on exposure to sunlight, and is more explosive than silver acetylide. The corresponding explosive copper derivative has also been prepared.

Chloroacetylene mixed with hydrogen reacts with a saturated aqueous solution of mercuric chloride, yielding *trichloromercuriacetic acid*, $\text{C}(\text{HgCl})_3 \cdot \text{CO}_2\text{H}$ (compare Abstr., 1905, i, 2), in the form of a crystalline powder, which is decomposed by hydrochloric acid, forming mercuric chloride and acetic acid. The acid dissolves in cold dilute potassium hydroxide solution, but, when heated, polymeric mercuriacetic acid is precipitated. When chloroacetylene is led into a solution of mercuric chloride and sodium acetate, a precipitate of *dischloromonohydroxy-trimercuriacetic acid*, $\text{OH} \cdot \text{Hg} \cdot \text{C}(\text{HgCl})_2 \cdot \text{CO}_2\text{H}$, is obtained. When dissolved in cold dilute potassium hydroxide solution and precipitated with carbon dioxide, *tri-hydroxymercuriacetic acid*,



is obtained as a yellowish-white powder.

When mercury chloroacetylide is shaken with a solution of mercuric chloride and sodium acetate, a precipitate, $\text{C}_4\text{H}_2\text{O}_2\text{Cl}_4\text{Hg}_3$, is thrown down.

J. J. S.

Halogen-amino-acids. VI. Iodo-derivatives of *p*-Toluidine.
3:5-Diiodo-4-aminobenzoic Acid. HENRY L. WHEELER and LEONARD M. LIDDLE (*Amer. Chem. J.*, 1909, 42, 441—461).—The only iodo-derivatives of *p*-toluidine hitherto described are the 2-iodo-derivative (Willgerodt and Gartner, Abstr., 1908, i, 876) and a di-iodo-derivative (Michael and Norton, Abstr., 1878, 407), which was regarded as the 3:5-compound. The corresponding di-iodo-derivative of *p*-aminobenzoic acid was also obtained by the latter authors. A study has now been made of these di-iodo-derivatives, and several other compounds have been prepared.

3-Iodo-*p*-toluidine, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{MeI}$, m. p. 40°, obtained by the interaction of molecular proportions of iodine and *p*-toluidine, forms colourless needles; the *hydrochloride*, m. p. 188° (decomp.), and the *osadate*, m. p. 119—120° (decomp.), are described. The *acetyl* derivative, m. p. 133°, crystallises in long, colourless prisms, and, when boiled with concentrated hydrochloric acid, yields 3:5-di-iodo-*p*-toluidine. The *benzoyl* derivative, m. p. 161°, forms long, colourless needles.

3-Iodo-*p*-tolylcarbamide, m. p. 187°, prepared by the action of potassium cyanate on 3-iodo-*p*-toluidine, forms thin, colourless plates. When 3-iodo-*p*-toluidine is heated with potassium thiobenzoate, benzenyl-4-amino-3-thiocresol (Hesse, Abstr., 1881, 597) is produced; its *platinichloride* crystallises with $1\text{H}_2\text{O}$.

3-Iodo-5(?)-nitroaceto-*p*-toluidide, $\text{NO}_2 \cdot \text{C}_6\text{H}_4\text{MeI} \cdot \text{NHAc}$, m. p. 202—203°, obtained by the action of nitric acid on 3-iodoaceto-*p*-toluidide, crystallises in prisms.

When *p*-toluidine (1 mol.) is warmed with iodine (2 mols.) in presence of water and calcium carbonate, 3:5-di-iodo-*p*-toluidine (Michael and Norton, *loc. cit.*) is produced; its *acetyl* derivative, m. p. 226°, forms stout, colourless prisms. 3:5-Di-iodotoluene, m. p. 44·5—45·5°, obtained by diazotising 3:5-di-iodo-*p*-toluidine in alcoholic solution and boiling the product, crystallises in yellow needles. 3:4:5-Tri-iodotoluene, m. p. 122—123°, prepared by the diazotisation of 3:5-di-iodo-*p*-toluidine dissolved in concentrated sulphuric acid, forms long, silky needles.

2-Iodo-3-nitrotoluene, $\text{NO}_2 \cdot \text{C}_6\text{H}_4\text{MeI}$, m. p. 67—68°, obtained by treating the product of the diazotisation of 3-nitro-*o*-toluidine with potassium iodide, crystallises in light yellow plates, and, on reduction with ferrous sulphate and ammonia, is converted into 2-iodo-*m*-toluidine, m. p. 41—42°, which forms long, flat prisms and yields an *acetyl* derivative, m. p. 135°. When the product of the diazotisation of 2-iodo-*m*-toluidine is treated with potassium iodide, 2:3-di-iodotoluene, m. p. 31—32°, is produced, which crystallises in colourless plates.

3-Iodo-4-acetylaminobenzoic acid, m. p. 230°, obtained by the oxidation of 3-iodoaceto-*p*-toluidide with potassium permanganate, forms long, colourless prisms. 2-Iodo-3-acetylaminobenzoic acid, m. p. 199°, prepared in a similar manner from 2-iodoaceto-*m*-toluidide, crystallises in prismatic needles. When 3-iodo-4-acetylaminobenzoic acid is boiled with concentrated hydrochloric acid, a mixture of *p*-aminobenzoic acid and 3:5-di-iodo-4-aminobenzoic acid is produced, the latter agreeing in properties with the compound obtained by Michael and Norton (*loc. cit.*) by the action of iodine monochloride on *p*-aminobenzoic acid. This compound can also be obtained, but only in poor yield, by the oxidation of 3:5-di-iodoaceto-*p*-toluidide with permanganate; its *ethyl* ester melts at 148°. 3-Iodo-4-aminobenzoic acid, m. p. 201—202°, is formed as an intermediate product in the preparation of 3:5-di-iodo-4-aminobenzoic acid by boiling 3-iodo-4-acetylaminobenzoic acid with hydrochloric acid, but is best prepared by the action of iodine monochloride on *p*-aminobenzoic acid. When potassium *p*-aminobenzoate is treated with iodine, *p*-iodoaniline is formed, but 3-iodo-4-aminobenzoic acid is not obtained. By the action of iodine on potassium 3:5-di-iodo-4-aminobenzoate, tri-iodoaniline, m. p. 184°, is produced.

3:4-Di-iodobenzoic acid, m. p. 257°, obtained by the action of potassium iodide on the product of the diazotisation of 3-iodo-4-aminobenzoic acid, crystallises in needles.

3:5-Di-iodobenzoic acid, m. p. 235°, prepared by the diazotisation of 3:5-di-iodo-4-aminobenzoic acid, forms pale yellow prisms.

3:4:5-Tri-iodobenzoic acid, m. p. 288°, obtained by adding potassium iodide to the product of the diazotisation of 3:5-di-iodo-4-aminobenzoic acid, crystallises in prismatic needles; its *sodium* salt crystallises with $2\frac{1}{2}\text{H}_2\text{O}$. 3:5-Di-iodo-4-hydroxybenzoic acid was also obtained from 3:5-di-iodo-4-aminobenzoic acid by means of the diazo-

reaction, but can be most conveniently prepared by the addition of iodine to a solution of *p*-hydroxybenzoic acid in potassium hydroxide. When dipotassium 3:5-di-iodo-4-hydroxybenzoate is heated with methyl iodide, *methyl 3:5-di-iodo-p-anisate*, m. p. 95°, is produced. 3:5-Di-iodo-*p-anisic acid*, m. p. 255—256° (decomp.), forms colourless prisms.

E. G.

Halogen-amino-acids. VII. Iodine Derivatives of *o*-Toluidine. 3-Iodoaminobenzoic Acids. HENRY L. WHEELER and LEONARD M. LITTLE (*Amer. Chem. J.*, 1909, 42, 498—505).—In an earlier paper (preceding abstract), it has been shown that by the action of iodine on *p*-toluidine, the 3-iodo- and 3:5-di-iodo-derivatives can be obtained.

A study has now been made of the action of iodine on *o*-toluidine, and it has been found that in this case only one derivative, namely, the 5-iodo-derivative (Artmann, *Abstr.*, 1905, i, 879), is formed, and that this can be melted with iodine without further substitution being effected.

2:5-Di-iodotoluene, m. p. 30—31°, obtained by the action of potassium iodide on the product of the diazotisation of 5-iodo-*o*-toluidine, forms long, colourless plates; its *acetyl* derivative, m. p. 169°, and *benzoyl* derivative, m. p. 184°, crystallise in colourless needles. By the oxidation of the *acetyl* derivative with potassium permanganate, 5-iodo-2-*acetylaminobenzoic acid*, m. p. 235° (decomp.), is produced, which forms colourless needles, and, when warmed with hydrochloric acid, is converted into 5-iodo-2-aminobenzoic acid, m. p. 209—210°, which is identical with Grothe's β -iodoaminobenzoic acid (*Abstr.*, 1879, 378). It follows from this that Grothe's α -iodo-amino- and α -iodonitro-benzoic acids are the 3-iodo-2-amino- and 3-iodo-2-nitro-derivatives and that his β -iodonitrobenzoic acid is the 5-iodo-2-nitro-compound. 3-Iodo-5-nitrobenzoic acid, m. p. 167°, prepared from 3-amino-5-nitrobenzoic acid (Hübner, *Abstr.*, 1884, 315) by means of the diazo-reaction, forms long, slender, pale yellow needles; this compound is not identical with Grothe's γ -iodonitrobenzoic acid (*loc. cit.*), and the latter must therefore be the 3-iodo-4-nitro-derivative. 3-Iodo-5-aminobenzoic acid, m. p. 197°, obtained by reducing 3-iodo-5-nitrobenzoic acid with ferrous sulphate and ammonia, forms long, pale yellow crystals; its *hydrochloride* has been prepared. On adding potassium iodide to the product of the diazotisation of 3-iodo-5-aminobenzoic acid, 3:5-di-iodobenzoic acid is produced, identical with that obtained by the authors (*loc. cit.*) from 3:5-di-iodo-4-aminobenzoic acid.

E. G.

Nitration of Diethylaniline. PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 297—303. Compare *Abstr.*, 1909, i, 214).—A method of obtaining 3:4-dinitrodiethylaniline, 2:4-dinitrodiethylaniline, and 2:5-dinitrodiethylaniline from diethylaniline is described in detail.

3:4-Dinitrodiethylaniline, m. p. 95°, exists in a labile, yellow modification and a stable, orange form, also in an extremely labile, yellow form. It is converted by nitric acid (D 1.37) into 2:4:5-trinitro-

diethylaniline, m. p. 158° ; if the nitric acid employed contains nitrous acid, then 2:4:5-*trinitroethylaniline*, m. p. 175° , is formed; the latter substance may also be prepared from the diethyl compound by treatment with sulphuric acid and sodium nitrite.

2:5-*Dinitrodiethylaniline* forms red crystals, m. p. 76° .

W. H. G.

Colour and Constitution. ALFRED WERNER (*Ber.*, 1909, 42, 4324—4328).—The author discusses the nature of the linking whereby highly coloured additive compounds are formed from polynitro-compounds and aromatic hydrocarbons or aromatic bases. The part played by the polynitro-compound in the formation of the additive-compound may be attributable to (a) hydrogen, either hydroxylic (in nitrophenols) or nuclear (in trinitrobenzene, picryl chloride, etc.), (b) the benzene nucleus, in virtue of its unsaturated character, (c) the nitro-group. The first alternative is improbable, since colourless trinitromesitylene forms coloured additive compounds. The second is negated by the fact that chloropierin and tetranitromethane form coloured compounds with aromatic hydrocarbons and amines. Since the formation of the labile additive compounds cannot be determined by the principal valencies of the nitro-group, the important conclusion is drawn that the appearance of the colour must be conditioned in some way by the supplementary valencies of the nitro-group.

With regard to the influence of the aromatic hydrocarbon in the production of the coloured additive compound, it is shown that tetranitromethane dissolves unsaturated aliphatic hydrocarbons and also unsaturated aliphatic acids (excepting those containing the double linking in the α -position to the carboxyl group) with a yellow colour, whilst the paraffin hydrocarbons, and also stearic acid, form colourless solutions. Consequently the formation of the additive compound is connected with the unsaturation of a hydrocarbon; as far as can be judged at present, the intensity of the colour of the additive compound increases with the unsaturation of the hydrocarbon.

The additive compounds of nitro-compounds and hydrocarbons, therefore, are molecular compounds, the formation of which depends on saturation of the supplementary valencies between nitro-groups and unsaturated carbon atoms.

From the fact that tetranitromethane develops an intense dark brown coloration with trimethylamine, the author draws the conclusion that in the additive compounds of polynitro-compounds and amines the nitro-group is joined, not to unsaturated carbon atoms, but to the tervalent nitrogen.

C. S.

Electrolytic Reduction of 2-Nitrotoluene-4-sulphonyl Chloride. FRITZ FICHTER and WALTER BERNOULLI (*Ber.*, 1909, 42, 4308—4311).—Aromatic sulphonyl chlorides containing a nitro-group are reduced much more smoothly than the compounds described previously (*Abstr.*, 1907, i, 690), because the nitro-group is first reduced to an amino-group, and the resulting basic substance readily

dissolves in the cathodic acid liquor. Thus a suspension of 2-nitro-toluene-4-sulphonyl chloride in alcoholic sulphuric acid is readily reduced at a lead cathode below 20°, using a current density of 0.07 amperes per sq. cm., and one and a-half times the quantity of electricity theoretically required. The product is 2-aminotolyl 4-mercaptan sulphate, which readily changes to the sulphate of 2-aminotolyl 4-disulphide by keeping in a loosely closed vessel. 2-Aminotolyl 4-disulphide, m. p. 82°, forms almost colourless needles, and yields an acetyl derivative, m. p. 239°. C. S.

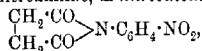
Nitration. VI. Nitroaniline Derivatives of Organic Acids. J. BISHOP TINGLE and C. E. BURKE (*J. Amer. Chem. Soc.*, 1909, 31, 1312—1319).—By the nitration of various *N*-acylanilides, Tingle and Blanck (Abstr., 1908, i, 778, 893) have prepared a large number of substances, the constitutions of some of which were not ascertained at the time, since their determination offered considerable difficulty. The present work was undertaken for the purpose of elucidating the structure of these compounds. Two series of experiments have been carried out; in the first series, *o*-, *m*-, and *p*-nitroanilines were treated at the ordinary temperature with various organic acids in presence of a solvent, whilst in the second series the mixture of acid and nitroaniline was fused, and the heating continued until the reaction was complete. The acids employed were formic, acetic, stearic, oxalic, succinic, tartaric, citric, benzoic, salicylic, phthalic, and picric acids. The nitration products of propionanilide were also investigated.

The product obtained by the nitration of propionanilide with nitric acid or a mixture of nitric and acetic acids has proved to be unchanged propionanilide, whilst the substance obtained by the action of a mixture of nitric and sulphuric acids is *p*-nitropropionanilide, m. p. 182°, which forms yellowish-brown plates.

Stearic acid does not unite with any of the nitroanilines; the products obtained by Tingle and Blanck in their attempts to nitrate stearanilide consisted of impure stearanilide.

Oxalic acid does not combine with the nitroanilines. The substances obtained by the action of nitric acid on oxalanilide prove to be impure oxalanilide. The yellow substance, prepared by the action of a mixture of nitric and oxalic acids on oxalanilide, was *p*-nitro-oxalanilide, m. p. 265°.

Succinic acid does not react with *o*- or *p*-nitroanilines, but on adding the acid to melted *m*-nitroaniline, *m*-nitrosuccinylphenylimide,



m. p. 172°, is obtained, which forms pale yellow crystals. The compound obtained by Tingle and Blanck on nitrating succinanil was the unchanged anil, whilst the compound prepared by the action of a mixture of nitric and oxalic acids on succinanilide was a dinitro-derivative, m. p. 240—243°.

Tartaric acid does not yield a compound with *o*-nitroaniline, but with *m*-nitroaniline it gives *m*-nitroaniline *m*-nitrophenylltartrate,

$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2, \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{H}$, m. p. 172°, in the form of small, yellow crystals, and with *p*-nitroaniline it gives *p*-nitrophenyltartramic acid,

$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{H}$, m. p. 218°, which forms bright yellow crystals. The compound obtained by Tingle and Blanck from tartranilide and a mixture of nitric and oxalic acids is found to be *s*-*m*-dinitrotartranilide,

$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, m. p. 224°.

Citric acid does not give derivatives with *o*- and *p*-nitroanilines, but with the *m*-compound yields a *di*-*m*-nitroaniline citrate, m. p. 267°. The compound obtained by Tingle and Blanck by the action of a mixture of nitric and oxalic acids on citranilide is *citryl tris*-*m*-nitroanilide, $\text{C}_3\text{H}_5\text{O}(\text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_3$, m. p. 122°. The other products obtained by the action of nitric acid on citranilide consisted of the impure anilide.

Salicylic and phthalic acids do not react with any of the nitroanilines. Benzoic acid yields small quantities of compounds when fused with *o*- and *m*-nitroaniline, but these have not been identified.

Picric acid does not react with *o*-nitroaniline, but yields the picrates of the meta- and para-isomerides, which have m. p. 147° and 100° respectively. The compound obtained by Tingle and Blanck by the action of a mixture of nitric and oxalic acids on picranilide is a *tetranitrodiphenylamine*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_4(\text{NO}_2)_3$, m. p. 197–200°; by the action of nitric acid on diphenylamine, another *tetranitrodiphenylamine*, m. p. 275°, is produced. F. G.

d-Leucyl-*l*-tryptophan. HANS FISCHER (*Ber.*, 1909, 42, 4320–4322).—Formyl-*l*-leucine is converted by Fischer's method (*Abstr.*, 1906, i, 808) into *l*-bromoisohexoic acid, and this by phosphorus pentachloride into *l*-bromoisohexoyl chloride, which is condensed with tryptophan (Abderhalden and Kempe, *Abstr.*, 1907, i, 652) to form *l*-bromoisohexoyltryptophan. This oily product is dissolved in 25% ammonium hydroxide, whereby *d*-leucyl-*l*-tryptophan,

$\text{C}_6\text{H}_5\text{N} \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}(\text{NH}_3) \cdot \text{C}_4\text{H}_9$, is obtained in needles. The dipeptide does not show the biuret reaction, has a sweet taste, is precipitated from acid solutions by phosphotungstic acid, and has $[\alpha]_D^{20} = -68.97^\circ$ in *N*-hydrochloric acid. It melts at 189° (corr.), but immediately crystallises to a substance, probably a tautomeride, melting at 225–230°, which can also be produced by crystallising the dipeptide from water, alcohol, and ether. Prepared by the latter method, the substance, $\text{C}_{17}\text{H}_{25}\text{O}_5\text{N}_2$, darkens at 230°, and has m. p. 243°; in *N*-hydrochloric acid it has $[\alpha]_D^{20} = -73.27^\circ$. C. S.

Maleic and Fumaric Derivatives of *p*-Aminophenols. ARNALDO PIUTTI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 312–326).—The theoretical part of this paper has been already published (*Abstr.*, 1908, i, 783), the author now giving the following experimental results.

p-Hydroxyphenylmaleinamic acid, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, prepared from *p*-aminophenol and maleic anhydride, separates in crusts of slender, yellow needles or in greenish-yellow prisms, m. p. 182° , and gives no coloration with ferric chloride.

p-Methoxyphenylmaleinamic acid, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, prepared from *p*-anisidine and maleic anhydride, crystallises in canary-yellow, dichroic needles or in yellow prisms exhibiting slight greenish-yellow pleochroism, m. p. 180 – 181° , and with ferric chloride gives a yellowish-brown coloration changing to violet.

p-Ethoxyphenylmaleinamic acid, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, prepared from *p*-phenetidine and maleic anhydride, crystallises in spherical aggregates of slender, yellow needles or in tufts of canary-yellow prisms, showing slight pleochroism, m. p. 181 – 182° (impure), and with ferric chloride gives a yellowish-brown coloration changing to intense violet.

p-Hydroxyphenylmaleimide, $\begin{array}{c} \text{CH}\cdot\text{C}(\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OH}) \\ | \\ \text{CH} \end{array} \text{---} \text{CO} \rangle \text{O}$, obtained by heating *p*-hydroxyphenylmaleinamic acid with acetyl chloride in acetone solution, separates in tufts or rosettes of acicular crystals, m. p. 154 – 155° .

p-Methoxyphenylmaleimide, $\text{C}_{11}\text{H}_9\text{O}_3\text{N}$, forms colourless, tubular crystals or small needles, m. p. 145 – 146° .

p-Ethoxyphenylmaleimide, $\text{C}_{12}\text{H}_{11}\text{O}_3\text{N}$, forms colourless, tubular crystals or silky needles, m. p. 127° , gives the normal molecular weight in freezing acetic acid, and, on reduction with sodium amalgam, yields *p*-ethoxyphenylsuccinamic acid and its imide (compare Abstr., 1896, i, 223). With aqueous or alcoholic sodium hydroxide it yields *p*-ethoxyphenylmaleinamic acid, whilst concentrated hydrochloric acid resolves it into *p*-aminophenol and fumaric acid. When treated with sodium ethoxide it gives the reddish-violet compound, $\text{C}_{11}\text{H}_{16}\text{O}_4\text{NNa}$, which, with sulphuric acid, yields the compound, $\text{C}_{14}\text{H}_{17}\text{O}_4\text{N}$, as a reddish-brown powder.

s-*p*-Methoxyphenylmaleimide, $\begin{array}{c} \text{CH}\cdot\text{CO} \\ | \\ \text{CH}\cdot\text{CO} \end{array} \rangle \text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, prepared by the action of phosphoric oxide on *p*-methoxyphenylmaleinamic acid, forms slender, yellow needles, m. p. 148.5° , and exhibits normal cryoscopic behaviour in acetic acid.

s-*p*-Ethoxyphenylmaleimide, $\text{C}_{13}\text{H}_{13}\text{O}_3\text{N}$, obtained from the corresponding amic acid by sublimation or by the action of phosphoric oxide, forms yellow needles, m. p. 134 – 135° , and has the normal molecular weight in freezing acetic acid.

p-Hydroxyphenylfumaric diamide, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, exists in two modifications: (1) white, decomp. at 220° , obtained by heating the acid fumarate of *p*-aminophenol at 200° in a current of carbon dioxide, and (2) yellow, which is obtained by crystallising the white variety from acetic acid, and is identical in properties with the white form.

p-Methoxyphenylfumaric diamide, $\text{C}_{18}\text{H}_{18}\text{O}_4\text{N}_2$, forms thin, white,

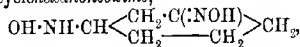
silky plates, m. p. 216°, and a yellow, apparently amorphous powder, having corresponding properties.

p-Ethoxyphenylfumaric diamide, $C_{20}H_{20}O_4N_2$, forms microscopic, colourless needles, m. p. 223°, and yellow, irregular plates, exhibiting marked pleochroism. T. H. P.

$\Delta^{1:2}$ -Dihydrophenol or Δ^2 -cycloHexenone. ARTHUR KÖTZ and TR. GRETHE (*J. pr. chem.*, 1909, [ii], 80, 473—510).— $\Delta^{1:2}$ -cycloHexadienol cannot be prepared from aliphatic compounds, but is obtained from cyclohexanone in several ways.

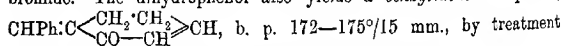
2-Chloro(or bromo)cyclohexanone is obtained by passing chlorine (or carbon dioxide charged with bromine vapour) into a mixture of cyclohexanone, calcium carbonate, and water at 25—30°; the chloro-derivative has m. p. 23°, b. p. 82°/13 mm., and the bromo-derivative has b. p. 89°/14 mm. $\Delta^{1:2}$ -cycloHexadienol is obtained from these compounds directly by heating with sodium acetate and glacial acetic acid or with ethereal aniline (best method), or indirectly by hydrolysing them by concentrated aqueous potassium hydroxide, the resulting cyclohexanone-2-ol, m. p. 92—92.5°, being converted into the dihydrophenol by anhydrous oxalic acid at 100—110°, or by Tschugaeff's xanthogenic reaction.

$\Delta^{1:2}$ -cycloHexadienol, b. p. 63°/14 mm., D^{20}_D 0.9868, n_D^{20} 1.4796, forms a semicarbazone, $C_7H_{11}ON_3$, m. p. 161°, and with 1 mol. of hydroxylamine hydrochloride an oxime, C_6H_9ON , m. p. 75—76°, which yields aniline by heating with acetic anhydride and then with sodium hydroxide. When the dihydrophenol is kept for eight days in a methyl-alcoholic solution of hydroxylamine (2 mols.), 3-hydroxyaminocyclohexanoneoxime,



m. p. 49—51°, is obtained, which dissolves in acids and in alkalis reduces warm Fehling's solution, and is oxidised by mercuric oxide in boiling water to cyclohexane-1:3-dioxime, m. p. 155.5°, which yields cyclohexane-1:3-dione, m. p. 105—106°, by hydrolysis by 10% sulphuric acid. 3-Hydroxyaminocyclohexanoneoxime is reduced by sodium and boiling alcohol to 1:3-diaminocyclohexane, the platinumchloride of which, $C_6H_{10}(NH_2)_2 \cdot H_4PtCl_6$, has m. p. 256° (decomp.).

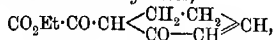
3-Chlorocyclohexanone, b. p. 91—92°/14 mm., is obtained by passing dry hydrogen chloride into a dry ethereal solution of $\Delta^{1:2}$ -cyclohexadienol. The dihydrophenol absorbs bromine, forming a dibromo-additive compound, which yields phenol by loss of 2 mols. of hydrogen bromide. The dihydrophenol also yields a benzylidene compound,



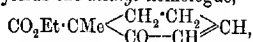
with benzaldehyde and cold alcoholic sodium ethoxide.

The action of carbon dioxide on an ethereal solution of $\Delta^{1:2}$ -cyclohexadienol in the presence of sodium leads to the formation of Δ^2 -cyclohexene-2-one-1-carboxylic acid ($\Delta^{1:2}$ -dihydrosalicylic acid), the ethyl ester of which, prepared from the silver salt, has b. p. 115—117°/15 mm. The constitution of the acid is proved as follows.

In the presence of sodium ethoxide, $\Delta^{1:3}$ -cyclohexadienol condenses with ethyl oxalate to form the *ethyl ester*,



which gives a red coloration with ferric chloride, and loses carbonic oxide by distillation in a vacuum, yielding ethyl $\Delta^{1:3}$ -dihydrosalicylate, b. p. $115^\circ/14$ mm. (blue colour with ferric chloride), identical with the preceding ester. Since by treatment with potassium and methyl iodide in xylene the ester yields the *methyl* homologue,



b. p. $110-125^\circ/12$ mm., which can be converted into 2-methylcyclohexanone, it must have the constitution assigned to it, and not that of Δ^6 -cyclohexen-2-one-1-carboxylic acid, m. p. 128° , which could not form a methyl derivative under the preceding conditions. This acid is obtained by heating ethyl 1-bromocyclohexan-2-one-1-carboxylate with sodium acetate and acetic acid, or the corresponding bromo-compound with ethereal aniline, and hydrolysing the *ethyl* Δ^6 -cyclohexen-2-one-1-carboxylate, b. p. $103^\circ/12$ mm., produced. It yields $\Delta^{1:3}$ -cyclohexadienol by distillation with soda-lime.

When an ethereal solution of cyclohexanone is gently boiled with sodanide and the resulting sodium derivative treated with carbon dioxide, cyclohexan-2-one-1-carboxylic acid is obtained ultimately; the *barium* and *silver* salts are mentioned, and the *ethyl ester* has b. p. $108-109^\circ/12$ mm.

Ethyl 4-methylcyclohexan-2-one-1-carboxylate yields ethyl 1-bromo-4-methylcyclohexan-2-one-1-carboxylate by bromination, which is boiled with ethereal aniline, whereby *ethyl* 4-methyl- Δ^6 -cyclohexen-2-one-1-carboxylate, b. p. $113^\circ/12$ mm., is produced; the corresponding acid has m. p. 153° , and by distillation with soda-lime yields 5-methyl- Δ^3 -cyclohexenone, b. p. 189° , which forms a *semicarbazone*, m. p. 158° .

G. S.

Synthesis of Octa-, Deca-, and Dodeca-methylene Compounds of the Aliphatic Series. JULIUS VON BRAUN [and A. TRÜMLER] (*Ber.*, 1909, 43, 4541-4554).—On coupling two molecules of phenyl δ -iodobutyl ether by means of sodium, *ab*-diphenoxyoctane is obtained in good yield, and the yield is increased when the same process is applied to the phenyl ethers of iodoamyl or iodoheptyl to form diphenoxy-decane and -dodecane derivatives. The further the iodine is distant from the phenoxy-group the more the compound tends to behave as a simple non-substituted alkyl iodide.

The replacement of the phenoxy-group by iodine, effected by heating with hydriodic acid in sealed tubes, becomes more difficult the larger the distance between the phenoxy-groups. Whereas diphenoxypentane only requires heating at 120° with 2 c.c. of fuming hydriodic acid per gram of ether, both diphenoxyhexane and diphenoxyoctane require heating at $130-135^\circ$ with 3 c.c. of the acid; diphenoxydecane must be heated at 150° with 4 c.c. of the halogen acid, and to convert diphenoxydodecane, it is necessary to heat with a large excess of

hydriodic acid at 175—180°. This method of preparing di-iodo-paraffins is not available much higher in the series.

Phenyl δ -iodobutyl ether is condensed in presence of sodium to *ab*-diphenoxyoctane, $\text{OPh} \cdot [\text{CH}_2]_6 \cdot \text{OPh}$ (compare Solonina, Abstr., 1899, i, 681), m. p. 80°, which, when heated with hydrogen iodide at 135°, forms *ab*-di-iodo-octane, $\text{I} \cdot [\text{CH}_2]_6 \cdot \text{I}$, b. p. 179—180°/13 mm.

ab-Diphenylthiooctane, $\text{C}_8\text{H}_{16}(\text{SPh})_2$, prepared by the interaction of di-iodo-octane, sodium, and thiophenol, is a colourless, crystalline solid, m. p. 83°.

ab-Dianilino-octane, $\text{C}_8\text{H}_{16}(\text{NHP})_2$, is formed quantitatively by the interaction of the iodide with aniline. It has m. p. 61—62°; the *picrate* and *nitroso*-derivative are oily; the *benzoyl* derivative has m. p. 110—112°.

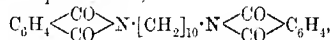
The condensation of phenyl ϵ -iodoamyl ether by sodium gives rise to compounds which may be separated by steam distillation into a volatile and a non-volatile product. The former, b. p. 117—120°/15 mm., consists of a mixture of phenyl-*n*-amyl ether and phenylamylethyl ether, $\text{CH}_3 \cdot \text{CH} \cdot [\text{CH}_2]_3 \cdot \text{OPh}$; when the mixture is heated with hydrogen iodide, *n*-amyl iodide, b. p. 62°/20 mm., and 1:4-di-iodopentane, b. p. 140°/20 mm., are obtained, the structure of the latter being proved by condensation with aniline to be phenyl-2-methylpyrrolidine (Scholtz and Friemehl, Abstr., 1899, i, 541), b. p. 136—138°/16 mm.; *picrate*, m. p. 108—109°; platinumchloride, m. p. 135°.

Amyl iodide, on prolonged heating with potassium cyanide, forms *hexonitrile*, a colourless liquid of penetrating, but not unpleasant, odour, b. p. 160°.

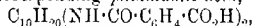
The non-volatile portion, *ak*-diphenoxylecane, has m. p. 85°; it yields *ak*-di-iododecane, $\text{C}_{10}\text{H}_{20}\text{I}_2$, a faintly-coloured oil, b. p. 212—215°/16 mm., which crystallises in very stable, lustrous, glass-like crystals, m. p. 29—30°. The corresponding *ak*-diphenylthiolecane has m. p. 85°.

Decane-*ak*-dicarboxylic acid, m. p. 125°, is identical with an acid described by Nördlinger (Abstr., 1890, 1237). The *nitrile*, prepared by heating di-iododecane with potassium cyanide, is a colourless, almost odourless liquid, m. p. 225—228°/17 mm., which solidifies when cooled with ice.

Di-iododecane, when heated with potassium phthalimide at 180—190°, forms a *phthalimide*,



m. p. 136°. The corresponding *phthalamic acid*,



separates in well-formed, colourless crystals, m. p. 129°. When the phthalimide is heated for four hours at 180° with hydrogen chloride, *ak*-diaminodecane, m. p. 60°, is formed. The *benzoyl* derivative has m. p. 152°.

Phenyliodohexyl ether is condensed by sodium to volatile products and *au*-diphenoxylodecane. It is converted with difficulty into *au*-di-iododecane, m. p. 41°.

When decane-*ak*-dicarboxylnitrile is reduced, the *hydrochloride* of *au*-diaminodecanesthane is formed; this does not melt at 250°; the

platinichloride, decomp. 225° . The free diamine is a colourless solid, m. p. $66-67^{\circ}$; the *benzoyl* derivative has m. p. 153° , and the *benzenesulphonyl* compound crystallises in nacreous plates, m. p. 99° .

E. F. A.

Monohalogenated Phenols. WILLIAM J. WOHLLEBEN (*Ber.*, 1909, 42, 4369—4375).—Commercial *o*-chlorophenol contains phenol, as it yields phenyl benzoate, m. p. 70° , on benzoylation. To purify it, it is conveniently shaken with an excess of potassium carbonate and the phenol present extracted with ether. *o*-Chlorophenyl acetate is a clear, colourless oil, b. p. $103^{\circ}/15$ mm., m. p. -20.5° to -19.5° , D_4^{20} 1.2166. *o*-Chlorophenyl *m*-nitrobenzoate crystallises in characteristic bunches of prisms, m. p. 98° .

m-Chlorophenyl acetate is an oil, b. p. $116.5^{\circ}/21$ mm., D_4^{20} 1.2209; it crystallises in needles, m. p. -1.5° to 0.5° ; the benzoate crystallises in glistening prisms, m. p. $71-72^{\circ}$; the *m*-nitrobenzoate separates in colourless, matted needles, m. p. $94-95^{\circ}$. *m*-Chlorophenetole (compare Guttermann, *Annalen*, 1907, 357, 349) is a clear oil with a pleasant odour; b. p. $204-205^{\circ}/717$ mm., D_4^{20} 1.1712. *o*-Chloro-*p*-hydroxyazobenzene, $\text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{Cl}\cdot\text{OH}$, crystallises in glistening, orange-red needles, m. p. $114-115^{\circ}$.

p-Chlorophenyl acetate is an oil, b. p. $108^{\circ}/12.5$ mm., D_4^{20} 1.2248; it forms long, crystal needles, m. p. $7-8^{\circ}$. All three chlorophenols dissolve when shaken with concentrated sodium carbonate, and are precipitated by carbon dioxide. *p*-Chlorophenyl *m*-nitrobenzoate forms lustrous, silky, concentrically grouped needles, m. p. 124.5° .

o-Bromophenyl acetate is a clear oil with an ethereal odour, b. p. $149-150^{\circ}$, D_4^{20} 1.4924.

m-Bromophenyl acetate has b. p. $149^{\circ}/40$ mm., D_4^{20} 1.5478. It does not mix with benzene; the benzoate crystallises in colourless, microscopic prisms or rhombic plates, m. p. 86° .

p-Bromophenyl acetate is an oil of unpleasant odour, b. p. $128^{\circ}/35$ mm., which forms colourless needles, m. p. 21.5° ; the benzoate, which has been variously described, crystallises from alcohol in colourless, rhombic plates, m. p. 104° .

p-Iodophenyl acetate forms colourless plates, m. p. $32-32.5^{\circ}$; the benzoate crystallises in colourless, six-sided or rhombic plates, or in matted needles, m. p. $118.5^{\circ}-119.5^{\circ}$; the *m*-nitrobenzoate separates in lustrous, long, colourless needles, m. p. $120-121^{\circ}$; the *benzenesulphonate* crystallises in long, colourless plates, or in bunches of lustrous, matted needles, m. p. $52-53^{\circ}$.

E. F. A.

Preparation of Aromatic Nitrohydroxy-compounds. RICHARD WOLFFENSTEIN and OSKAR BOETERS (*D.R.-P.* 214045. Compare Abstr., 1908, i, 629).—It has been shown previously that the action of nitric acid on aromatic hydrocarbons in the presence of mercury results in the formation of nitrohydroxylated products; it is now found that nitrous acid or the oxides of nitrogen react in a similar manner. The treatment of benzene with nitrogen peroxide in the presence of mercury yields 2:4-dinitrophenol, whilst with fuming nitric acid at a high temperature picric acid is obtained.

F. M. G. M.

Preparation of Arylalkyl-*p*-aminophenols. CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P. 213592. Compare Abstr., 1909, i, 914).—The following compounds prepared by the reduction (with zinc in alkaline solution) of the condensation products from substituted *p*-aminophenols and aromatic aldehydes are employed for photographic purposes.

3-Chloro-4-benzylideneaminophenol, m. p. 180—181°, from the condensation of benzaldehyde with 3-chloro-4-aminophenyl sulphate, yields, on reduction, *3-chloro-4-benzylaminophenol*, which was not obtained in crystalline form; its crystalline *hydrochloride* has m. p. 195° (decomp.).

4-Benzylideneamino-m-cresol, m. p. 133°, prepared from 4-amino-*m*-tolyl sulphate and benzaldehyde, yields, by reduction, *4-benzylamino-m-cresol*, which separates in the form of its sparingly soluble *sodium* salt; the *hydrochloride* has m. p. 220° (decomp.), and from this, on treatment with sodium sulphide, the free base, m. p. 84°, is obtained.

F. M. G. M.

Estimation of Ortho- and Para-Sulpho-groups in Phenol-sulphonic Acids. JULIUS OBERMILLER (*Ber.*, 1909, 42, 4361—4369).

—It is well known that by treatment with bromine, phenolsulphonic acids lose their *o*- and *p*-sulphonic groups, which are eliminated as sulphuric acid. The latter can be estimated gravimetrically, but to avoid too high results the following directions must be closely followed.

The bromine solution consists of water containing 1 per cent. of sodium bromate (or 1.1% of potassium bromate) and 5% of potassium bromide; it contains 3.1—3.2% of potential bromine. The phenol-sulphonate, 0.2 to 0.3 gram, with three times the weight of barium chloride, and 10 c.c. of hydrochloric acid, D 1.19, are diluted to 100 c.c. with water. The solution is heated to 60—65°, and slowly treated, with certain precautions, with the bromine solution until a faint persistent, yellow colour is produced. A little alcoholic phenol is added to absorb the excess of bromine, and then sufficient alcohol to dissolve the tribromophenol. The liquid is boiled and decanted while warm from the barium sulphate, which is repeatedly washed in the beaker with 50% alcohol and then with hot water. The barium sulphate is finely filtered and weighed in the usual way. Barium *o*-phenolsulphonate, magnesium *p*-phenolsulphonate, and barium phenol-2:4-disulphonate (Abstr., 1907, i, 910) have been satisfactorily treated by this process, although the results are still a little high. Sulpho-groups in the para-position are eliminated with greater difficulty than those in the ortho-position. Of the salts of doubtful constitution, previously obtained by the fractional crystallisation of the salts prepared from the sulphonation products of phenol (*loc. cit.*), the "aluminium salt of the para-acid" proves to be the magnesium salt, the "magnesium salt of the ortho-acid" to be the magnesium salt of the para-acid, the "barium salt of the ortho-acid" to be barium chloride, and the "magnesium salt of the disulphonic acid" to be a mixture of calcium phenol-2:4-disulphonate and magnesium *o*-phenolsulphonate.

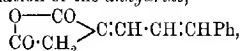
C. S.

Abnormal Reduction of an Aromatic Nitro-compound with Tin and Hydrochloric Acid and an Interesting Case of Dimorphism. OTTO DE VRIES (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 305—306; *Rec. trav. chim.*, 1909, 28, 395—407).—3-Nitro-4-methoxytoluene, when reduced with iron and acetic acid, yields the corresponding amine, whilst treatment with tin and hydrochloric acid leads to the formation of 6-chloro-3-amino-*p*-tolyl methyl ether, which forms colourless needles, m. p. 106° (corr.); the acetyl derivative has m. p. 115° (corr.). In order to arrive at the constitution of the compound, it was converted into 3:6-dichloro-*p*-tolyl methyl ether, which was obtained in a labile modification, crystallising in needles, m. p. 23°, and a stable modification, forming flat crystals, m. p. 44°. The fused substance, when cooled, yields the labile variety, which, by inoculation or in an infected region, passes spontaneously into the stable form.

W. H. G.

2:5-Diphenylphenol. FRITZ FICHTER and OTTO WALTER (*Ber.*, 1909, 42, 4311—4313).—2:5-Diphenylphenol (*Abstr.*, 1903, i, 481) yields 2:5-diphenylphenyl *p*-toluenesulphonate, $C_{25}H_{20}O_3S$, m. p. 102°, by boiling with alcoholic potassium hydroxide, and *p*-toluenesulphonyl chloride. *p*-Nitrobenzeneazodiphenylphenol, $OH \cdot C_6H_4 \cdot Ph_2 \cdot N_2 \cdot C_6H_4 \cdot NO_2$, red needles, decomposing at 243—245°, is obtained by the action of diazotised *p*-nitroaniline on alcoholic diphenylphenol in alkaline solution.

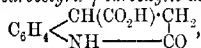
The attempt to produce a benzene ring by the condensation of styrylitaconic acid (*Abstr.*, 1901, i, 594) by acetic anhydride at 130° resulted in the formation of the anhydride,



m. p. 180°.

The nitration of phenylsuccinic acid by nitric acid, D 1.52, at 0° results in the formation of *o*-nitrophenylsuccinic acid, m. p. 188°, and *p*-nitrophenylsuccinic acid, m. p. 218°—220° (decomp.); *p*-acetylamino-phenylsuccinic acid has m. p. 218°.

The reduction of *o*-nitrophenylsuccinic acid by ammoniacal ferrous sulphate yields dihydrocarbostyryl- γ -carboxylic acid,



m. p. 573°, which separates from water in colourless needles. C. S.

The Fluorene Series. I. JULIUS SCHMIDT and HERMANN STÜTZEL (*Annalen*, 1909, 370, 1—40. Compare *Abstr.*, 1908, i, 415; Schmidt and Mezger, *Abstr.*, 1907, i, 43; Schmidt and Söll, *ibid.*, 1054).—Although fluorenoneoxime is converted by zinc and acetic acid into 9-aminofluorene, when it is reduced by tin and hot concentrated hydrochloric acid it yields fluorenyl ether, the formation of which may be explained thus: $C_6H_5 > C:NOH \rightarrow C_6H_5 > CO \rightarrow C_6H_5 > CH \cdot OH \rightarrow C_6H_5 > CH \cdot O \cdot CH < C_6H_5$. The most remarkable property of this substance is its red colour, which cannot be due to a

quinonoid structure, for fluorene and 9-hydroxyfluorene are quite colourless, but is probably the result of an accumulation of benzene nuclei.

It is shown that the known 9-hydroxyfluorene is directly connected with α -9-aminofluorene, since it yields α -9-acetoxyluorene when heated with acetic anhydride; attempts to prepare the 9-hydroxyfluorene, corresponding with β -9-aminofluorene, were unsuccessful.

When 9-acetylaminofluorene is warmed with nitric acid, it yields 1:8-dinitrofluorenone, many derivatives of which have been prepared. The behaviour of 1:8-dinitrofluorenone towards stannous chloride and hydrochloric acid is remarkable, in that a nitro-group is eliminated with the formation of 1-amino-9-hydroxyfluorene, a compound not without interest, for it is red, and the substances derived from it are also intensely coloured. When 1:8-dinitrofluorenoneoxime is reduced with tin and hydrochloric acid, it likewise yields 1-amino-9-hydroxyfluorene, but when treated with zinc dust and acetic acid it is converted into 1:9-diaminofluorene.

Fluorenyl ether crystallises in red prisms, m. p. 254—255°, and when warmed with concentrated nitric acid yields a yellow substance, m. p. about 285°.

α -9-Hydroxyfluorene, m. p. 153°, is obtained by the action of nitrous acid on either α - or β -9-aminofluorene, possibly because β -9-hydroxyfluorene is labile and passes into the stable α -form; the *benzoate*, $C_{20}H_{14}O_2$, crystallises in colourless leaflets, m. p. 161°.

When 9-aminofluorene is reduced with amyl alcohol and sodium, it yields an oily substance, which is either 9-aminodihydrofluorene or 9-aminotetrahydrofluorene; the *picrolonate* forms yellow crystals, m. p. 218°; attempts to reduce 9-aminofluorene with hydrogen in the presence of platinum-black were unsuccessful.

1:8-Dinitrofluorenone, $\begin{array}{c} \text{CH} \cdot \text{C}(\text{NO}_2) \cdot \text{C} \cdot \text{CO} \cdot \text{C} \cdot \text{C}(\text{NO}_2) \cdot \text{CH} \\ | \\ \text{CH} - \text{CH} = \text{C} - \text{C} = \text{CH} - \text{CH} \end{array}$ crystallises in glistening, yellow prisms, m. p. 196—197°, and is oxidised by potassium permanganate, yielding *o*-nitrobenzoic acid; the *phenylhydrazone*, $C_{15}H_{13}O_4N_4$, forms scarlet needles, m. p. 206—207°; the *semicarbazone*, $C_{14}H_{13}O_3N_3$, is a brownish-yellow powder, which does not melt at 300°.

1:8-Dinitrofluorenoneoxime, $C_{13}H_9O_3N_3$, crystallises in pale yellow nodules, m. p. 250°; the *benzoyl* derivative, $C_{20}H_{11}O_6N_3$, forms pale yellow needles, m. p. 218—220°; the *acetyl* derivative, $C_{15}H_9O_5N_3$, crystallises in brownish-yellow needles, m. p. 178°; the *methyl ether*, $C_{14}H_9O_3N_3$, forms small, pale yellow, crystalline nodules, m. p. about 150° (decomp.).

1-Amino-9-hydroxyfluorene, $C_{13}H_{11}ON$, crystallises in dark red needles, m. p. 142°; the *acetyl* derivative, $C_{15}H_{13}O_2N$, forms small, brownish-yellow crystals, m. p. 200°; the *benzoyl* derivative,

$C_{20}H_{15}O_2N$, crystallises in flesh-coloured needles, m. p. 260°; the position of the acyl group in the compounds just described is not known; the *hydrochloride*, $C_{13}H_{11}ON \cdot HCl$, forms small, brownish-yellow crystals, m. p. 290° (decomp.); the *nitrate* forms small, brown crystals, and

does not melt at 300° ; the *picrolonate*, $C_{23}H_{19}O_6N_3$, forms greenish-yellow crystals, m. p. 246° (decomp.); the *additive* product with phenylcarbimide, $C_{27}H_{21}O_5N_3$, forms small, red crystals, m. p. 262° . The *diazo*-derivatives couples with phenols and amines, yielding *azo*-dyes, and when boiled with water yield 1:9-*dihydroxyfluorene*, a reddish-brown, crystalline substance, m. p. $218-220^{\circ}$; the *diacetate* crystallises in reddish-brown needles, and does not melt at 300° .

1:9-*Diaminofluorene*, $C_{13}H_{13}N_2$, forms small, white crystals, m. p. about 120° ; the *diacetyl* derivative, $C_{17}H_{15}O_2N_2$, crystallises in white leaflets, m. p. 293° ; the *dibenzoyl* derivative, $C_{27}H_{20}O_2N_2$, forms small, white needles, m. p. about 310° ; the *picrate* crystallises in greenish-yellow leaflets, m. p. 205° (decomp.); the *picrolonate*,

$C_{23}H_{20}O_5N_3$, forms yellowish-brown crystals, and decomposes at about 235° ; 1:9-*diphenylcarbamidofluorene*, prepared from the diamine and phenylcarbimide, forms small, white crystals, m. p. $258-260^{\circ}$.

W. H. G.

Cholesterol. I. The Xanthogen Reaction. LEO TSCHUGAEFF and A. GASTEFF (*Ber.*, 1909, 42, 4631-4634).—The authors have applied the xanthogen reaction (Abstr., 1900, i, 129; 1905, i, 71) to cholesterol. In order to avoid molecular rearrangement in the formation of potassium cholesteroxide, the compound was prepared by the action of a toluene solution of cholesterol on potassium anyloxide.

Methyl cholesterylcanthate, $C_{27}H_{45}O \cdot CS \cdot SMe$, is prepared by adding an excess of carbon disulphide to potassium cholesteroxide, and then warming with methyl iodide or sulphate. It crystallises in colourless needles, m. p. 126° , and has $[\alpha]_D - 39^{\circ}$ in 9% toluene solution. When heated, it begins to decompose at 260° , yielding methyl hydrosulphide, carbonyl sulphide, and a hydrocarbon, *cholesterylene*, $C_{27}H_{44}$. This forms colourless needles, m. p. 77° , and has $[\alpha]_D - 107^{\circ}$ in 11% toluene solution. It decolorises bromine, and gives the usual cholesterol reactions.

J. J. S.

Preparation of Cholesteryl α -Bromoisovalerate. CHEMISCHE WERKE FORM. DR. HEINRICH BYK (D.R.-P. 214157).—*Cholesteryl α -bromoisovalerate*, m. p. $132-133^{\circ}$, results from the action of α -bromoisovaleryl chloride on a mixture of cholesterol and diethylaniline in dry benzene; it is insoluble in water, and has no taste. The ester is hydrolysed by aqueous alkalis; these properties render it a valuable therapeutic agent.

F. M. G. M.

Phytosterols in the Family of Synantheraea. Faradiol, a New Dihydric Alcohol from Coltsfoot. TIMOTHÉE KLOBB (*Compt. rend.*, 1909, 149, 999-1001. Compare Abstr., 1903, i, 165; 1904, i, 410; 1905, i, 594).—The following substances have been isolated from the flowers of *Tussilago farfara*: (1) a saturated hydrocarbon, m. p. about 57° ; (2) a *phytosterol*, having m. p. about 127° , and forming an *acetate*, m. p. $117-119^{\circ}$, $[\alpha]_D - 36.7^{\circ}$ in chloroform; (3) a viscous, yellow substance; (4) a dihydric alcohol, *faradiol*, $C_{30}H_{50}O_2$ (or $C_{31}H_{52}O_2$ or $C_{29}H_{48}O_2$). This crystallises from alcohol in large,

efflorescent, ortho-rhombic prisms, containing 1 mol. of alcohol and having m. p. 209—211°; after removal of alcohol, m. p. about 238°. $[\alpha]_D + 45.1^\circ$ in acetone. It gives Liebermann's reaction, developing a strawberry-red coloration with a green fluorescence. The acetate has m. p. 140—145°, $[\alpha]_D + 63.6^\circ$, and appears to exist in two modifications; the propionate crystallises in pearly lamellae, m. p. 155—158°, $[\alpha]_D + 62.3^\circ$ in benzene. The phenylurethane, $C_{44}H_{60}O_4N_2$, crystallises in prisms, and becomes pasty at 190—205°.

W. O. W.

Dehydration of cycloHexanolpropan- β -ol. P. JOSEPH TARBURIECH (*Compt. rend.*, 1909, 149, 862—864. Compare Abstr., 1909, i, 796).—When cyclohexanolpropan- β -ol is heated with sulphuric acid (20%), a hydrocarbon, C_9H_{14} , is produced (together with a mixture of polymerides), and a pinacoline, $C_9H_{16}O$. The hydrocarbon is a very mobile liquid, b. p. 76°/19 mm. which combines with bromine and forms a hydrochloride, b. p. 96—98°/20 mm., and a dihydrochloride, b. p. 122—123°/18 mm. The ketone is separated by submitting the mixture to Crismer's method of oximation, when two isomeric compounds are obtained and separated by crystallisation from absolute alcohol; the α -oxime has m. p. 83°, the β -oxime, m. p. 45°; when these are treated with phenylcarbimide, they form two carbanilino-oximes; the α -derivative occurs in silky needles, m. p. 79—80°, the β -derivative forms hard crystals, m. p. 94—95°.

When regenerated from the mixed oximes, the ketone is obtained as a liquid, b. p. 83°/18 mm., having a camphoraceous odour; the α -semicarbazone forms needles, m. p. 158°, whilst the β -semicarbazone has m. p. 176°.

When the dehydration is effected by anhydrous oxalic acid, the same products are formed, but in different proportions.

W. O. W.

New Method of Preparation of Tricyclenecarboxylic Acid (Dehydrocamphenylic Acid). JULIUS BREDT and R. MAY (*Chem. Zeit.*, 1909, 33, 1265).—A 70—80% yield of tricyclenecarboxylic acid is obtained as follows: 50 grams of camphenylic nitrite (compare Jagelki, Abstr., 1899, i, 627) are added in small portions to 250 c.c. of concentrated sulphuric acid at 0°, the resulting product is poured on to 750 grams of ice, and the liquid submitted to steam distillation. The formation of the acid is accompanied by that of two lactones, m. p. 137° and 198°.

W. II. G.

Preparation of *n*-Propyl *p*-Aminobenzoates. FRANZ FRITZSCHE & Co. (D.R.-P. 213459).—The anæsthetic action of the alkyl *m*- and *p*-aminobenzoates is increased by replacing methyl and ethyl with propyl as the ester-forming alkyl group. Further increase in anæsthetic action is not, however, observed when higher alkyl, hydroaromatic, or aromatic groups are employed, but rather an increase in toxicity.

n-Propyl *p*-aminobenzoate is prepared by condensing *n*-propyl alcohol and *p*-nitrobenzoic acid by means of sulphuric acid, and reducing the *n*-propyl *p*-nitrobenzoates with tin and hydrochloric acid; the latter compound forms yellow, rhombic plates, and melts at 35°. The

amino-ester is also produced directly by treating *p*-aminobenzoic acid with *n*-propyl alcohol and either sulphuric acid or hydrogen chloride. It forms needles, m. p. 73—74°.

F. M. G. M.

Isomerism by Anils (Schiff's Bases). WILHELM MANCHOT and J. R. FURLONG (*Ber.*, 1909, 42, 4383—4389).—Whereas ethyl *o*-hydroxybenzylidene-*p*-aminobenzoate exists in two isomeric forms (*Abstr.*, 1909, i, 805), only one form of the corresponding methyl ester can be obtained, and the two isomerides of the free acid could not be separated.

Methyl o-hydroxybenzylidene-*p*-aminobenzoate forms colourless, hexagonal crystals, m. p. 145°; they become dark red when heated above 100°, but immediately assume the original faint yellow colour when cooled.

o-Hydroxybenzylidene-*p*-aminobenzoic acid forms a mass of yellow or orange-red needles, which consist of almost colourless, hexagonal crystals mixed with more highly-coloured needles. When allowed to crystallise from, or heated with, amyl alcohol above 100°, the crystals become red, but lose their colour on cooling. The solid when heated becomes red at 90°, orange at 160°, sealing-wax red at 220°, bluish-red at 250°; m. p. 259° to a dark red liquid, which on cooling solidifies first to a red and finally to a yellow mass.

When exposed to light it rapidly becomes orange-red, but loses the colour again in the dark. When cooled in liquid air it becomes almost colourless.

The *hydrochlorides* of both yellow and red modifications of ethyl *o*-hydroxybenzylidene-*p*-aminobenzoate, prepared by interaction with hydrogen chloride in boiling benzene solution (yellow form) or in ethereal solution at -15° (red form), are yellow, crystalline precipitates, both m. p. 175—180° and very similar. When powdered with water, however, that from the yellow form regenerates this substance, whilst that from the red product gives a red substance, which becomes yellow at 83°, m. p. 87°. The two hydrochlorides must therefore be regarded as different.

p-Hydroxy-*m*-methoxybenzylidene-*p*-aminobenzoic acid is an amorphous substance, m. p. 209°. When heated with water it forms a red oil solidifying to red needles, which when dried lose their crystalline character. The colour vanishes at 75—77°, and the product has m. p. 200°.

Ethyl p-hydroxy-*m*-methoxybenzylidene-*p*-aminobenzoate forms glistening, faint yellow plates, m. p. 149°. It gives rise to a red, crystalline substance when treated with water and a little hydrogen chloride. The *hydrochloride* has m. p. 213—217°.

The following anils are also described; in no case were two isomerides obtained:

p-Hydroxy-*m*-methoxybenzylidene-*o*-toluidine is colourless, m. p. 115°.

p-Hydroxy-*m*-methoxybenzylidene-*p*-toluidine crystallises in well-formed, colourless columns, m. p. 117°.

p-Methylbenzylidene-*p*-aminobenzoic acid forms colourless crystals, m. p. 241°.

p-isopropylbenzylidene-*p*-aminobenzoic acid yields citron-yellow crystals, m. p. 245°.

3 : 4-Methylenedihydroxybenzylidene-*p*-aminobenzoic acid yields a bright yellow, crystalline mass, m. p. 242°.

Benzylidene-*p*-aminobenzoic acid gives colourless crystals, m. p. 193.5°.

p-Hydroxybenzylidene-*o*-toluidine has m. p. 169.5°.

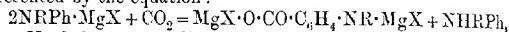
Ethyl *p*-hydroxybenzylidene-*p*-aminobenzoate forms a bright yellow or almost colourless mass of glistening plates, m. p. 174.5°. The methyl ester separates in almost colourless needles, m. p. 189°.

o-Methoxybenzylidene-*p*-aminobenzoic acid forms faintly yellow-coloured crystals, m. p. 227°; the ethyl ester has m. p. 166°.

E. F. A.

Synthesis of Aromatic Amino-acids by Rearrangements.

III. Alkylaminotoluic Acids. JOSEF HOUBEN, ARNOLD SCHOTT-MÜLLER, and ROBERT FREUND (*Ber.*, 1909, **42**, 4488—4496).—By the rearrangement, under certain conditions, of phenylcarbamates containing an alkyl group united with the nitrogen into aminobenzoates (compare Abstr., 1904, i, 1014; 1909, i, 921), the authors have succeeded in extending Kolbe's hydroxybenzoic acid synthesis to the corresponding amino-compounds. In the latter case, the yield of amino-acid never exceeds about 40%, and the final reaction must be represented by the equation:



where X = halogen, according to which the maximum possible yield is 50%, which has now been nearly approached.

The reaction has been applied to methylamino- and ethylamino-*o*-toluene, both of which give *p*-carboxylic acids, but the highest yields obtained are only about 12%, owing to the sensitiveness of the aminotoluic acids or their salts to the high temperatures at which they are formed. In the syntheses effected with the alkylanilines, considerable proportions of tertiary amino-acids were often obtained, but with the alkyltoluidines, even when large amounts of dialkyltoluidine are added, only the secondary amino-acids are obtained; these can be characterised by conversion into nitroaminic acids, or where this presents complications, into the acetyl derivatives by shaking the aqueous solutions of the alkali salts with acetic anhydride.

In the preparation of the aminotoluic acids, just as with the aniline-carboxylic acids, carbamide-like compounds are always formed in large or small proportion.

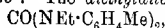
A secondary aminotoluic acid is obtained also when, in place of methylamino-*o*-toluene, a mixture of *o*-toluidine and dimethylamino-*o*-toluene is employed, so that either the *o*-toluidine undergoes methylation or the dimethylamino-*o*-toluene, demethylation.

6-Methylamino-*m*-toluic acid, $\text{NHMe} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CO}_2\text{H}$, prepared by treating a mixture of *o*-toluidine and *o*-dimethylaminotoluene with magnesium and ethyl iodide in ethereal solution, and subsequently passing carbon dioxide through the liquid, forms long, white needles,

m. p. 201°. *Ditolylmethylcarbamide* (?), $C_6H_5Me \cdot NH \cdot CO \cdot NMe \cdot C_6H_4Me$, also formed in this reaction, has m. p. 238°.

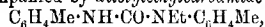
6-*Methylnitrosoamino-m-toluic acid*, $NO \cdot NMe \cdot C_6H_3Me \cdot CO_2H$, forms yellow needles, m. p. 153°.

6-*Ethylamino-m-toluic acid*, $NH_2Et \cdot C_6H_3Me \cdot CO_2H$, prepared from α -ethylaminotoluene and ethyl iodide, forms white needles, m. p. 169—170°, and gives salts with both alkalis and mineral acids. The acetyl derivative, $NEtAc \cdot C_6H_3Me \cdot CO_2H$, has m. p. 228°. 6-*Ethyl-nitrosoamino-m-toluic acid*, $NO \cdot NEt \cdot C_6H_3Me \cdot CO_2H$, forms long, yellow needles, m. p. 135°. The *diethylditolylcarbamide* (?),



formed together with 6-ethylamino-m-toluic acid, forms long, white needles, and carbonises on heating.

4-*Ethylamino-m-toluic acid*, $NH_2Et \cdot C_6H_3Me \cdot CO_2H$, prepared from p -ethylaminotoluene and ethyl iodide, crystallises in yellow leaflets, m. p. 191°. The contiguity of the ethylamino- and carboxyl groups is indicated by the intense, bluish-violet fluorescence (similar to that shown by anthranilic acid) exhibited by aqueous and alcoholic solutions of the acid; this fluorescence disappears on addition of dilute acetic acid, apparently owing to salt formation, the basicity of the ethylamino-group being possibly increased by the methyl group in the para-position. The corresponding *nitroso-acid*, m. p. 184° (impure), was obtainable only in small quantity. The ethylamino-toluic acid is accompanied by *ditolylethylcarbamide* (?),



m. p. 233°.

T. H. P.

Addition of Ethyl Phenylacetate to Unsaturated Compounds. WALTHER BORSCHKE (*Ber.*, 1909, 42, 4496—4499).—In the author's investigations on the reactivity of the methylene group in the nitro-derivatives of ethyl phenylacetate (*Abstr.*, 1909, i, 233, 385), it was found that these compounds do not readily form additive compounds with ethylene linkings. Sodium ethoxide attacks them rapidly, with destruction of the methylene group, whilst, under the influence of piperidine at 100°, addition occurs very slowly and imperfectly. With ethyl phenylacetate itself, however, in spite of its slight reactivity compared with the nitro-derivatives, addition takes place readily with $\alpha\beta$ -unsaturated ketones and carboxylic esters in presence of sodium ethoxide. If ketones containing a methylene group are employed, ring-closure with loss of alcohol occurs under the influence of the sodium ethoxide, the resulting compounds being phenyl derivatives of dihydrosorcinol.

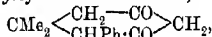
Ethyl $\alpha\beta$ -diphenylglutarate, $CO_2Et \cdot CHPh \cdot CHPh \cdot CH_2 \cdot CO_2Et$, prepared from ethyl phenylacetate and ethyl cinnamate, forms colourless needles, m. p. 92—93°. The free *acid*, $C_{17}H_{16}O_4$, forms colourless needles, m. p. 230—231°.

The nitrile of α -phenylcinnamic acid does not form an additive compound with ethyl phenylacetate under the conditions employed.

Ethyl γ -benzoyl- $\alpha\beta$ -diphenylbutyrate, $CO_2Et \cdot CHPh \cdot CHPh \cdot CH_2 \cdot Bz$, prepared from ethyl phenylacetate and benzylideneacetophenone,

forms white, silky needles, m. p. 153—154°; the corresponding acid is obtained as a white powder, m. p. about 240°.

2-Phenyl-1:1-dimethylcyclohexan-3:5-dione,



prepared from ethyl phenylacetate and mesityl oxide, forms colourless leaflets containing $1\text{H}_2\text{O}$, m. p. about 135° (anhydrous).

1:2-Diphenylcyclohexan-3:5-dione, $\text{CHPh} \begin{array}{c} \diagup \text{CH}_2 - \text{CO} \\ \diagdown \text{CHPh} \cdot \text{CO} \end{array} \text{CH}_2$, obtained, together with a resinous polymeride of benzylidenacetone, by the interaction of the latter and ethyl phenylacetate, forms colourless leaflets, m. p. 159—160°.

T. H. P.

allo- and iso-Cinnamic Acids. CARL LIEBERMANN and H. TRUCKSÄSS (*Ber.*, 1909, 42, 4659—4674. Compare Abstr., 1909, i, 155; also Biilmann, *ibid.*, i, 155, 382).—The authors give full particulars of the precautions necessary when working with one of these acid in order to avoid inoculation with particles of one of the isomeric acids. The hands, corks, and filter-papers are washed with alcohol and ether, and all glass vessels are "sterilised" by heating for some time at 105°.

In the preparation of the *iso*-acid, m. p. 42°, by fusing the *allo*-acid at 105°, and cooling in a flask fitted with a sterile cork, it is an advantage to work with small amounts (0.5 gram) at a time, since, with larger quantities, it is more difficult to destroy all particles of the *allo*-acid, and on solidification the minute particles left cause the separation of crystals of *allo*-acid. The *iso*-acid can be crystallised from light petroleum, b. p. 30—50°, or even b. p. 60—70° if proper precautions are taken. The acid is characterised by its rhombic crystals, their elastic nature, the soapy feel of the crystals when rubbed with a pestle, and their planes of cleavage.

No trustworthy method of obtaining the *iso*-acid, m. p. 58°, without inoculation with a particle of the acid is known.

The three acids when converted into calcium salts by shaking with water and powdered marble, and then precipitated with dilute hydrochloric acid, gave the original acid. This may be due to the fact that small particles of the original acid were not transformed into the calcium salt, and when acidified served as nuclei which produced the separation of the acid in question.

The three acids were converted into aniline salts; in each case the aniline salt had the same m. p., namely, 83—84° (Erlenmeyer, *sen.*, Abstr., 1896, i, 46). The acid was recovered from the aniline salt by the following three methods: 1. Precipitation of the hot aqueous solution of the salt with excess of hydrochloric acid, filtering and washing the precipitate, and extracting the mother liquor with ether. 2. Rubbing the dry salt with very dilute hydrochloric acid and extracting with ether. 3. Rubbing the salt with dilute alkali, removing the aniline with ether, acidifying the alkaline liquid, and extracting the acid with ether.

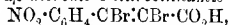
By the first method, all three acids gave the *iso*-acid, m. p. 58°, with

the exception of one experiment, when the *iso*-acid, m. p. 42°, was obtained. Method 2 gave varying results. Method 3 gave either *allo*-acid or *iso*-acid, m. p. 42°.

The *iso*-acid, m. p. 58°, and the *allo*-acid can be converted into the *iso*-acid, m. p. 42°, by boiling with very dilute hydrochloric acid, and cooling in a flask provided with a cotton-wool plug.

One of the best methods of transforming the *allo*-acid or *iso*-acid, m. p. 58°, into the more fusible *iso*-acid is to dissolve in excess of sodium hydroxide solution, and, after two hours, to precipitate with hydrochloric acid (D 1.1). If precautions are taken, the acid which separates is always the *iso*-acid, m. p. 42°. J. J. S.

Bromination of *o*-Nitrophenylpropionic Acid. GUSTAV HELLER and WALTER TISCHNER (*Ber.*, 1909, 43, 4566—4568).—By the action of bromine vapour, or of an excess of bromine in benzene on *o*-nitrophenylpropionic acid, $\alpha\beta$ -dibromo-*o*-nitrocinnamic acid,



is formed in small quantity mixed with nitrocinnamic acid. The dibromo-acid crystallises in stellate aggregates of colourless, lustrous needles, m. p. 222° (decomp.).

Bromination in glacial acetic acid solution leads to the formation of $\alpha\alpha\beta\beta$ -tetra bromo-*o*-nitrophenylethane, $\text{NO}_2\cdot\text{C}_6\text{H}_3\cdot\text{CBr}_2\cdot\text{CHBr}_2$, which crystallises in rectangular, glistening, yellow plates, m. p. 186°.

E. F. A.

Preparation of *o*- ω -Trichloroacetoxybenzoic Acid. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 213591. Compare Abstr., 1909, i, 798).

—*o*- ω -Trichloroacetoxybenzoic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{CCl}_3$, can be prepared by treating salicylic acid or its salts with trichloroacetic anhydride or trichloroacetyl chloride in the presence of a tertiary base, such as dimethylaniline. It forms colourless crystals, m. p. 150—152°. The acid chloride or anhydride can be replaced by the free acid if phosphorus trichloride or phosphoric oxide is also employed. The chlorination of *o*-acetoxybenzoic acid leads to substitution in the phenyl nucleus instead of in the side-chain.

F. M. G. M.

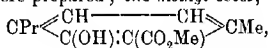
Preparation of Aromatic Halogenalkyloxycarboxylic Acids. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 213593).—It has been found that when the tolyl halogen alkyl ethers are oxidised with either permanganate, manganese dioxide with sulphuric acid, or dichromate and sulphuric acid they yield the corresponding carboxylic acids without any loss of halogen from the alkyloxy-group.

p-Bromoethoxybenzoic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_2\text{H}_4\text{Br}$, colourless, glistening leaflets, m. p. 178°, is thus prepared from *p*-tolyl bromoethyl ether; the ethyl ester has m. p. 76°.

o-Bromoethoxybenzoic acid, from *o*-tolyl bromoethyl ether, melts at 164°.

F. M. G. M.

Preparation of *o*-Thymotic Acid and of Certain of its Derivatives. ROSARIO SPALLINO and G. PROVENZAL (*Gazzetta*, 1909, 39, ii, 325—336).—By the action of sodium on a xylene solution of thymol through which a current of carbon dioxide was passed, the author has prepared *o*-thymotic acid, which forms monoclinic crystals [ROSATI, $a:b:c = 1.0724:1:0.9039$; $\beta = 93^\circ 24'$, m. p. 127°. Kolbe and Lautomann (*Annalen*, 1860, 115, 205) and Kobek (*Abstr.*, 1884, 56) gave 120°, and Puxeddu (*Abstr.*, 1906, i, 995), 123°. The *silver* and *sodium* salts were prepared; the *methyl* ester,



b. p. 142°/18.5 mm., and the *ethyl* ester, $\text{C}_{13}\text{H}_{18}\text{O}_3$, b. p. 153°/18.5 mm., are pale yellow, oily liquids.

The action of phosphoric oxide or phosphoryl chloride on *o*-thymotic acid in xylene solution yields a mixture of two isomeric thymotides (compare Naquet, *Bull. Soc. chim.*, 1863, 4, 96; 1865, 6, 98). The *first*, $\text{C}_{22}\text{H}_{24}\text{O}_4$, forms colourless, rhombohedral crystals (ROSATI, $a:c = 1:1.1092$; $a = 94^\circ 11'$, m. p. 174°, and is hydrolysed readily by alcoholic potassium hydroxide, and more slowly by concentrated sulphuric acid, yielding *o*-thymotic acid; the *second* isomeride, m. p. 209°, forms biaxial crystals, and is readily hydrolysed by alcoholic potassium hydroxide or concentrated sulphuric acid. The two thymotides exhibit different solubilities in various solvents, but both give normal molecular weights in freezing benzene or phenol. They are probably stereoisomerides of the structure:

$$\begin{array}{c} \text{CH:CMc}\cdot\text{C}\cdot\text{CO}\cdot\text{O}\cdot\text{C}\cdot\text{CPr}\cdot\text{CH} \\ \text{CH}\cdot\text{CPr}\cdot\text{C}\cdot\text{O}\cdot\text{CO}\cdot\text{C}\cdot\text{CMc}\cdot\text{CH} \end{array}$$

T. H. P.

Action of Free Hydroxylamine on Coumarin. LUIGI FRANCESCONI and GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 183—188).—The authors traverse the statement made by Posner (*Abstr.*, 1909, i, 583) that the dihydroxylaminohydrocoumarin described by them (*ibid.*, i, 233) is a mixture of β -hydroxylaminodihydrocoumarohydroxamoxime hydroxide and β -aminodihydrocoumaric acid (termed aminohydrocoumaric acid by the present authors).

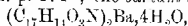
Further experiments show that at 0° coumarin takes up 3 mols. of hydroxylamine, giving β -hydroxylaminodihydrocoumarohydroxamoxime hydroxide, m. p. 128°. At the ordinary temperature (20—25°), that is, under the conditions in which 1 mol. of hydroxylamine is added to the lactonic linking of santonin, only 2 mols. of hydroxylamine are added to coumarin, the resultant product being dihydroxylaminohydrocoumarin, m. p. 130—131°, which is far more stable than β -hydroxylaminodihydrocoumarohydroxamoxime hydroxide. At the b. p. of methyl alcohol, either no reaction occurs or aminohydrocoumaric acid is formed.

T. H. P.

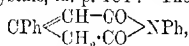
Anhydrides of *iso*Phthalic and Terephthalic Acids. JOHN E. PUCHER and W. CLIFTON SLADE (*J. Amer. Chem. Soc.*, 1909, 31, 1319—1321).—It has been stated in certain well known text-books that *isophthalic* and *terephthalic* acids cannot form anhydrides. It

has been found, however, that the anhydrides of both acids can be obtained by dissolving the acids in acetic anhydride and distilling off the liquid at 200°. The *anhydrides* are thus obtained as granular substances, which decompose on heating without showing definite m. p., are not volatile, and are readily soluble in warm solutions of alkali hydroxides. The properties of these compounds indicate that they have a high molecular weight, and may be represented by the formula $[C_6H_4(CO)_2O]_x$. E. G.

β -Phenylglutaconic Acid. FRANZ FEIST and G. POMME (*Annalen*, 1909, 370, 72—81. Compare this vol., i, 7).— β -Phenylglutaconic acid, prepared by any one of the known methods (compare Michael, Abstr., 1894, i, 172; Ruhemann, Trans., 1899, 75, 248; Buchner and Schroeder, Abstr., 1902, i, 319), is obtained in one modification only, m. p. 154—155°, which is regarded by Buchner and Schroeder as the *cis*-form, because of its close relationship to the anhydride; this view, however, is shown to be incorrect; the acid, m. p. 154—155°, must have the *trans*-configuration, for the anhydride when acted on by alkali in the presence of casein yields on precipitation with silver nitrate a silver salt, which, when suspended in ether and decomposed by hydrogen sulphide, yields the anhydride, whereas, in the absence of casein, the acid, m. p. 154°, is obtained; the presence of the anti-catalyst prevents the transformation of the labile *cis*-isomeride into the *trans*-acid, but the former, being unstable, passes into the anhydride. The crystalline barium and calcium salts were analysed. The *semi-anilide*, $C_{17}H_{15}O_3N$, prepared from the anhydride and aniline, forms pearly crystals, m. p. 174°; the barium salt,



was analysed; the corresponding *semi-p-toluidide*, $C_{15}H_{13}O_3N$, forms aggregates of pearly crystals, m. p. 184°. The *anil*,



obtained by the action of aniline on the acid at 130°, crystallises in colourless needles, m. p. 232°; the corresponding *p-tol'id*, $C_{15}H_{15}O_3N$, crystallises in needles, m. p. 248·5—249°.

β -Phenyl- α -benzylglutaconic acid, $CO_2H \cdot CH(CH_2Ph) \cdot CPh \cdot CH \cdot CO_2H$, prepared by the action of benzyl chloride and sodium ethoxide on ethyl β -phenylglutaconate at 110° under pressure, is an oil; the barium and silver salts were analysed.

Ethyl β -phenylglutaconate, when heated with benzaldehyde and an alcoholic solution of potassium hydroxide, yields **β -phenyl- α -benzylideneglutaconic acid**, $CO_2H \cdot C(CHPh) \cdot CPh \cdot CH_2 \cdot CO_2H$, crystallising in compact needles, m. p. 210·5°.

β -Phenylglutaconic acid does not combine with hydrogen bromide, but absorbs bromine slowly, yielding **$\alpha\beta$ -dibromo- β -phenylglutaric acid**, $CO_2H \cdot CHBr \cdot CPhBr \cdot CHBr \cdot CO_2H$, which forms crystals, m. p. 166° (decomp.). W. H. G.

Action of Sulphuric Acid on Santonin. II. GUIDO BARGELLINI and S. SILVESTRI (*Gazzetta*, 1909, 39, ii, 346—349. Compare Abstr., 1909, i, 723).—The authors have investigated the products obtained

by the action of sulphuric acid (D 1.5) on santonin at various temperatures. At the ordinary temperature (about 20°), *l*-desmotroposantonin is formed; at 30–60°, a mixture of *l*-desmotroposantonin and desmotroposantonin, and at 50–90°, a mixture of desmotroposantonin, $[\alpha]_D + 112^\circ$, *d*-santonous acid, and a red, tarry matter. At 100°, no desmotroposantonin is formed, the product consisting entirely of *d*-santonous acid and the red tar. Desmotroposantonin is converted into these two substances by the action of sulphuric acid (D 1.5) at 100°, and hence forms the first product of the action of the acid on santonin, its conversion into santonous acid by reduction being probably accompanied by a corresponding oxidation to a ketosantonous acid, thus: $\text{:CH}\cdot\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{:CH}_2$ (santonous acid) and $\text{:CH}\cdot\text{OH} + \text{O} = \text{H}_2\text{O} + \text{:CO}$ (ketosantonous acid). The red, tarry matter is being investigated in order to ascertain whether it contains a ketosantonous acid.

The action of syrupy phosphoric acid (D 1.725) on santonin is similar to that of sulphuric acid (D 1.5). T. H. P.

Benzaldehydesulphoxylates. MAX BAZLEN (*Ber.*, 1909, 42, 4634–4637. Compare Abstr., 1905, ii, 240).—In reply to Fromm and Erfurt (Abstr., 1909, i, 936), the author gives full details for the preparation of sodium benzaldehydesulphoxylate, $\text{NaHSO}_3\cdot\text{C}_6\text{H}_5\cdot\text{CHO}$, from sodium hyposulphite, sodium hydroxide solution, and benzaldehyde. The yield is almost theoretical, and the product can be crystallised from hot water containing a little sodium hydroxide, when it forms well developed crystals. The analogous zinc compound, $\text{Zn}(\text{HSO}_3\cdot\text{C}_6\text{H}_5\cdot\text{CHO})_2\cdot 4\text{H}_2\text{O}$, can be obtained by shaking benzaldehyde with a warm solution of zinc hyposulphite. It also forms well developed crystals. These primary salts are very unstable in contact with the air. Secondary salts have also been prepared, and are more stable. *Disodium benzaldehydesulphoxylate*, $\text{Na}_2\text{SO}_3\cdot\text{C}_6\text{H}_5\cdot\text{CHO}\cdot 2\text{H}_2\text{O}$, forms colourless needles, and can be obtained by the action of sodium hydroxide solution on the primary sodium salt. The *barium* and *zinc* salts have been prepared. J. J. S.

Preparation of *p*-Methoxysalicylaldehyde from *p*-Hydroxysalicylaldehyde. KALLE & Co. (D.R.-P. 214153).—*p*-Methoxysalicylaldehyde was only obtained in small yield from resorcinol monomethyl ether by the Tiemann reaction owing to its instability. It has now been found possible to prepare it in a stable, pure condition by methylating *p*-hydroxysalicylaldehyde with methyl sulphate or methyl halide at 70–80° in the presence of aqueous sodium carbonate. The pure product melts at 41°, not at 62–63°, and, contrary to the statements in the literature, is readily soluble in water, particularly on warming. F. M. G. M.

New Syntheses of Vanillin. ALFRED GUYOT and A. GRY (*Compt. rend.*, 1909, 149, 928–931. Compare Abstr., 1909, i, 236, 306, 935).—An application of the general method for the preparation of aldehydes described previously (Abstr., 1909, i, 933) to the synthesis of vanillin. The following compounds are prepared by the

condensation of mesoxalic esters or of $\alpha\beta$ -diketonic esters with guaiacol.

Methyl p-hydroxy-m-methoxyphenyltartronate,
 $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{C}(\text{OH})(\text{CO}_2\text{Me})_2$,
 prisms, m. p. 115° ; the *ethyl* ester crystallises in long needles, m. p. 64° . *Ethyl p-hydroxy-m-methoxyphenylacetylglucollate*,
 $\text{C}_6\text{H}_3\text{O}_2\cdot\text{CAc}(\text{OEt})\cdot\text{CO}_2\text{Et}$,
 prisms, m. p. 61° . *Ethyl p-hydroxy-m-methoxyphenylbenzoylglucollate*,
 $\text{C}_6\text{H}_3\text{O}_2\cdot\text{CBz}(\text{OH})\cdot\text{CO}_2\text{Et}$, prisms, m. p. 139° .

The esters are converted into vanilloylcarboxylic acid by one of the methods mentioned previously (*loc. cit.*). A quantitative yield of pure vanillin is obtained when the acid is heated at 170° with an equal weight of dimethyl-*p*-toluidine (compare Gassmann, Abstr., 1907, i, 343).

The $\alpha\beta$ -diketonic esters employed in this synthesis can be replaced by the corresponding acids. The yield of vanillin, however, is diminished, thus dihydroxytartaric acid gave only 15% of the weight of guaiacol employed. W. O. W.

Organic Syntheses by Means of Sunlight. IV. Action of Paraffins and Homologues of Benzene on Ketones and Aldehydes. EMANUELE PATERNO and G. CHIEFFI (*Gazzetta*, 1909, 39, ii, 415—435. Compare Abstr., 1909, i, 393, 487).—The interaction of benzophenone and pentane under the influence of sunlight results in the formation of benzopinacolone and a resin, which may be a polymeric of the characteristic compound of benzophenone and anylene (*loc. cit.*).

Benzophenone and octane yield benzopinacolone and a resin, which was not identified.

Benzophenone and decane (*diisocamyl*) give benzopinacolone and a resinous *additive* compound, $\text{C}_{12}\text{H}_{10}\text{O}\cdot\text{C}_{10}\text{H}_{20}$.

In general, then, aliphatic hydrocarbons are transformed by the action of benzophenone into unsaturated hydrocarbons, which yield additive compounds with the benzophenone: $3\text{C}_{15}\text{H}_{10}\text{O} + \text{C}_n\text{H}_{2n+2} = \text{C}_{26}\text{H}_{22}\text{O}_2 + \text{C}_{15}\text{H}_{10}\text{O}\cdot\text{C}_n\text{H}_{2n}$; these additive compounds are resins, and are decomposed into their constituents on heating.

Benzaldehyde and pentane yield hydrobenzoin (I) and polymeric of benzaldehyde, similar results being obtained with benzaldehyde and octane or decane and with *p*-tolualdehyde and octane.

With certain cyclic hydrocarbons, such as cyclohexane or methyl- or dimethyl-cyclohexane, benzophenone yields benzopinacolone and a resin which has not yet been investigated.

Benzophenone and benzene do not seem to react under the influence of sunlight. Benzophenone and toluene yield benzopinacolone and an *additive* compound, $\text{C}_{20}\text{H}_{18}\text{O}$, m. p. 79 — 82° , probably analogous to that formed by benzophenone and benzyl alcohol (compare Hell and Wiegandt, Abstr., 1904, i, 490).

Benzophenone and ethylbenzene give: (1) benzopinacolone; (2) a compound, m. p. 87 — 89° , probably $\text{OH}\cdot\text{CPh}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{Ph}$, which has the normal molecular weight in freezing benzene, and, when

treated with phosphoric oxide, yields the *triphenylpropylene*,
 $\text{CPh}_3\cdot\text{CH}\cdot\text{CH}_2\text{Ph}$,

m. p. $87-89^\circ$; (3) a hydrocarbon, m. p. $124-125^\circ$, probably dimethyldibenzyl (compare Moritz and Wolfenstein, Abstr., 1899, i, 424).

Benzophenone and propylbenzene yield benzopinacone and a *con. pound*, $\text{C}_{15}\text{H}_{10}\text{O}\cdot\text{C}_3\text{H}_7$ (or $\text{C}_{12}\text{H}_{10}\text{O}\cdot\text{C}_3\text{H}_{10}$), m. p. $94-96^\circ$, which, with phosphoric oxide, gives an *anhydride*, m. p. $80-81^\circ$ and not a hydrocarbon.

Benzophenone and *p*-xylene give benzopinacone and di-*p*-methyldibenzyl (compare Moritz and Wolfenstein, Abstr., 1899, i, 910).

Benzophenone and cymene yield benzopinacone, a hydrocarbon with an unsaturated chain, and a resin, now under examination.

Benzophenone and oil of turpentine give benzopinacone and a viscous oil, b. p. $230-320^\circ$, which yields benzophenone on distillation.

Benzophenone and diphenylmethane yield $\alpha\alpha\beta\beta$ -tetraphenylethanol, $\text{CHPh}_2\cdot\text{CPh}_2\cdot\text{OH}$, which forms monoclinic crystals [ZAMBONINI: $\alpha:b:c=2.9673:1:3.0298$; $\beta=91^\circ50'$], m. p. $212-214^\circ$, and has the normal molecular weight in boiling alcohol or benzene; when treated with phosphoric oxide, or with phosphorus and iodine, it yields *s*-tetraphenylethane.

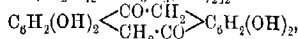
With benzaldehyde and toluene, dibenzyl or diphenylmethane, no reaction occurs, the benzaldehyde undergoing rapid polymerisation. Anisaldehyde and toluene yield hydroanisoin and a resin, not yet examined. With oil of turpentine and benzaldehyde, *isohydrobenzoin* is formed. T. H. P.

2:4:6-Tribromobenzophenone. P. J. MONTAGNE (*Rec. trav. chim.*, 1909, 28, 449-455. Compare Abstr., 1908, i, 988).—It is shown that the yellow product formed when 2:4:6-tribromobenzophenone is heated is 6:8-dibromofluorenone. 2:4:6-Tribromobenzophenone is reduced to 4-bromobenzhydrol when heated with sodium hydroxide in alcohol. The latter reaction to some extent negatives the suggestion of Diels and Rhodius (Abstr., 1909, i, 351), that since the carbonyl group of ketones is reduced by sodium amyloxide, but not by sodium ethoxide, some specific action must be exerted by the amyl group in the former reagent. The author finds in fact that benzophenone is readily reduced either by potassium hydroxide or sodium hydroxide in alcohol.

6:8-Dibromofluorenone, m. p. 225° , b. p. 430° (decomp.), crystallises in slender needles from alcohol; on reduction with sodium amalgam it yields fluorene alcohol, and on oxidation with sulphuric acid and mercuric sulphate, it furnishes phthalic anhydride. T. A. H.

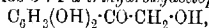
Derivatives of Catechol. HUGO VOSWINCKEL (*Ber.*, 1903, 42, 4651-4654. Compare Dreczowski, *J. Russ. Phys. Chem. Ges.*, 1893, 25, 157).—Chloroacetocatechol diacetate, $\text{C}_6\text{H}_3(\text{OAc})_2\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$, has m. p. 110° , not 95° , and 3:4-diacetoxyacetophenone, m. p. 87° , not 78° .

In the preparation of chloroacetocatechol a small amount of a higher condensation product, $C_6H_4[CO \cdot C_6H_3(OH)_2]_2$ or

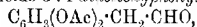


is obtained when phosphoryl chloride is used. It crystallises in glistening, silver, hexagonal plates, m. p. 261° . Its *tetra-acetyl* derivative, $C_{24}H_{20}O_{10}$, crystallises from nitrobenzene in rhombic plates, m. p. 253° .

3:4: α -Triacetoxyacetophenone, $C_6H_3(OAc)_2 \cdot CO \cdot CH_2 \cdot OAc$, obtained by heating chloroacetocatechol (α -chloro-3:4-dihydroxyacetophenone) with acetic anhydride and dry potassium acetate, crystallises in plates, m. p. 94° , and when hydrolysed with alcoholic sodium hydroxide solution yields 3:4- α -trihydroxyacetophenone,



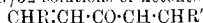
which crystallises in colourless prisms, m. p. 195° . When reduced with zinc dust and glacial acetic acid, the triacetoxy-derivative yields 3:4-diacetoxyphenylethyl acetate, $C_6H_4(OAc)_2 \cdot CH_2 \cdot CH_2 \cdot OAc$, which crystallises in colourless plates, m. p. 85° . When heated with acetic anhydride and potassium acetate, or when heated alone at 130° , the triacetoxy-derivative yields 3:4-diacetoxyphenylacetaldehyde,



and acetaldehyde. The former crystallises in large, thin plates, m. p. 88° , and yields a crystalline phenylhydrazone. J. J. S.

Relationship between the Colour and Constitution of Unsaturated Ketones and Their Salts. HANS STOBBE (*Annalen*, 1909, 370, 93—99).—A brief account of the nature and results of the investigations described in the following papers. W. H. G.

Light Absorption, Basicity, Constitution, and Salts of Ketones of the Dibenzylideneacetone [Distyryl Ketone] and Dibenzylidenecyclopentanone Series. HANS STOBBE and RICHARD HAERTEL (*Annalen*, 1909, 370, 99—129).—I. *Colour of Ketones of the Dibenzylideneacetone and Dibenzylidenecyclopentanone Types*.—The absorption spectra of $N/32$ solutions of ketones of the types



and $\begin{array}{c} CH_2 \cdot C(:CHR) \\ CH_2 \cdot C(:CHR') \end{array} \rangle CO$ in chloroform have been measured, where

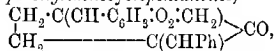
RR' = benzylidene, 4-methoxybenzylidene, cuminylidene, 2-ethoxybenzylidene, 3:4-dimethoxybenzylidene, piperonylidene, cinnamylidene, or furfurylidene; R = benzylidene and R' = 4-methoxybenzylidene, or R = benzylidene and R' = piperonylidene.

The results obtained may be summarised thus: (1) The absorption band is shortest when RR' = benzylidene. (2) Each replacement of a phenyl hydrogen atom by an alkyl or alkyloxy-group is accompanied by an increase in the length of the absorption band; the influence exerted in the ortho-position is smaller than in the para-position; the compounds in which RR' = 3:4-dimethoxybenzylidene and piperonylidene have the greatest absorption. (3) Stereoisomerides, such as the stereoisomeric benzylidenecinnamylidenecyclopentanones (compare Abstr., 1909, i, 309), exhibit different absorption. (4) The colour intensity

is increased by the addition of ethylene linkings; thus, replacement of benzylidene by cinnamylidene is accompanied by a great increase in the length of the absorption band. (5) Comparison of the spectra of the corresponding acetone and cyclopentanone compounds shows that the absorption bands of the latter are about 10μ longer than those of the former.

Di-3:4-dimethoxystyryl ketone, $[C_6H_3(OMe)_2 \cdot CH:CH]_2CO$, prepared by the interaction of 3:4-dimethoxybenzaldehyde and acetone in a dilute alcoholic solution of sodium hydroxide, forms golden-yellow crystals, m. p. 84° . *Di-2-ethoxybenzylidenecyclopentanone*, $C_{22}H_{24}O_2$, prepared in a similar manner, has m. p. 110° ; the corresponding *di-3:4-dimethoxybenzylidene* compound, $C_{22}H_{24}O_2$, has m. p. 195.5° .

Benzaldehyde, piperonaldehyde, and cyclopentanone interact in a dilute alcoholic solution of sodium hydroxide, yielding two stereoisomeric *benzylidenepiperonylidenecyclopentanones*,



obtained as lemon-yellow crystals, m. p. 176° , and deep lemon-yellow crystals, m. p. 192° , respectively.

II. *Colour of the Crystalline Chloro-, Dichloro-, and Trichloro-acetates of the Ketones.*—The colour relationship existing between the ketones is found to exist also between the salts. The acid salts are more intensely coloured than the neutral salts. The colour intensity also increases with the strength of the acid. In the following list of salts, K represents one mol. of the ketone and A one mol. of the acid.

Distyryl ketone trichloroacetate, KA, lemon-yellow, m. p. 117° ; *dichloroacetate*, KA, pale yellow.

Di-4-methoxystyryl ketone trichloroacetate, KA, vermilion, m. p. 93° ; K2A, carmine, m. p. 63° ; *dichloroacetate*, KA, orange-yellow, m. p. 96° ; K2A, orange-red, m. p. 92° ; *chloroacetate*, K4A, orange-yellow, m. p. 45° .

Di-2-ethoxystyryl ketone dichloroacetate, K2A, orange-red, m. p. 33° .

Di-3:4-dimethoxystyryl ketone trichloroacetate, KA, brown, m. p. 105° ; *dichloroacetate*, KA, orange-yellow, m. p. 87° .

Dipiperonylidenecetone trichloroacetate, K2A, garnet-red, m. p. 87° ; *dichloroacetate*, KA, light brown, m. p. 100° .

Styryl 4-methoxystyryl ketone trichloroacetate, KA, orange-red, m. p. 66° ; *dichloroacetate*, KA, light yellow, m. p. 48° .

Dicinnamylidenecetone trichloroacetate, K2A, black, m. p. 110° ; *dichloroacetate*, K2A, very dark red, m. p. 56° ; *chloroacetate*, K6A, orange-yellow, m. p. 56° .

Dibenzylidenecyclopentanone trichloroacetate, K2A, straw-yellow, m. p. 98° ; *dichloroacetate*, KA, sulphur-yellow, m. p. 110° ; *chloroacetate*, sulphur-yellow, m. p. 75° .

Di-4-methoxybenzylidenecyclopentanone trichloroacetate, K2A, garnet-red, m. p. 73° ; *dichloroacetate*, KA, orange-yellow, m. p. 133° ; K2A, scarlet, m. p. 85° ; *chloroacetate*, K5A, orange-red, m. p. 48° .

Dipiperonylidenecyclopentanone trichloroacetate, K4A, black, m. p. $85-90^\circ$; KA, orange, m. p. 148° .

Benzylidenecinnamylidenecyclopentanone, m. p. 147° ; *trichloroacetate*,

K2A, lemon-yellow, m. p. 97°; *dichloroacetate*, KA, lemon-yellow, m. p. 68°.

Dicinnamylidenecyclopentanone trichloroacetate, K2A, black, m. p. 80°; *dichloroacetate*, KA, orange-red, m. p. 158°.

Difurfurylidenecyclopentanone trichloroacetate, K2A, black, m. p. 82°; *dichloroacetate*, KA, orange-red, m. p. 158°.

III. *Colour and Composition of the Hydrochlorides of the Ketones at 15° and -75°*.—The absorption of hydrogen chloride by the solid ketone has been investigated with the following results: (1) As a rule, at 15°, 1–2 mols., and at -75°, 4–6 mols., of hydrogen chloride are absorbed; the alkyloxy-derivatives combine with a greater proportion of hydrogen chloride than the alkyl compounds; stereoisomethides combine with the same amount of hydrogen chloride. (2) The relationships between colour and constitution observed in the case of the salts with the chloroacetic acids also exist in the case of the hydrochlorides.

IV. *Absorption Spectra of Certain Salts of the Ketones dissolved in Various Acids*.—The absorption spectra of equivalent solutions of the various ketones in sulphuric, phosphoric, chloroacetic, dichloroacetic, trichloroacetic, formic, and acetic acids, and in chloroform have been measured. It is found that the colour of solutions of the same ketone becomes more intense as the strength of the acid increases; the solutions in acetic acid are of approximately the same intensity as in chloroform, indicating the presence of only traces of acetate. It is clear that the colour of the solution depends, not only on the specific colour of the salt, but also to a great extent on the degree of hydrolysis of the salt. The effect of the constitution of the ketone on the colour of the solution remains more or less constant.

V. *Relationship between Basicity of the Ketone and the Colour of Certain Salts of the Ketones*.—The basicity of the various ketones has been determined. It is found that (1) derivatives of dibenzylidenecetone and dibenzylidenecyclopentanone, obtained by substituting phenyl hydrogen atoms, are more basic than the parent substances; isopropyl has the smallest effect; dioxymethylene (CH_2O_2), ethoxy- (EtO), and methoxy- (MeO) groups increase the basicity in the order given; the basic character is also increased by substituting furyl and cinnamyl for phenyl; (2) the basicity of a cyclopentanone compound is about two-thirds of that of the corresponding acetone compound; (3) replacement of benzylidene by *p*-methoxybenzylidene and piperonylidene increases the basicity by 2.4 and 1.7 times respectively; the basicity is roughly doubled by replacing one benzylidene group by a cinnamyl group; (4) a relationship appears to exist between the light absorption and basicity of the ketones.

W. H. G.

Light Absorption, Basicity, Constitution, and Salts of Certain Unsaturated Cyclic Ketones, Ketone Acids, and Ketone-Esters. HANS STOBBE and SIEGFRIED SEYDEL (*Annalen*, 1909, 370, 129–141).—An investigation on the colour relationships existing between fluorenone, fluorenone-4-carboxylic acid, and ethyl fluorenone-4-carboxylate; *allochryso*ketonecarboxylic acid and the ethyl ester; dibromoinidone, phenylindonacetic acid, and the ethyl ester.

Fluorenone is lighter in colour than the carboxylic ester, and this again lighter than the acid. The solutions of these substances in sulphuric, trichloroacetic, dichloroacetic, and chloroacetic acids are red or dark yellow, the intensity of the solution of the same substance increasing with the strength of the acid. The solutions of the three compounds in the same acid are of unequal colour-tone, and, unlike the free substances, the solution of the ketone is darker than that of the ester, and this darker than the solution of the acid. The explanation of this is, that the ketone is more basic than the ester, which is more basic than the acid.

The other ketonic substances investigated were found to give the same results; the intensity of the solution in an acid depends both on the strength of the acid and the basicity of the ketone.

Ethyl fluorenone-4-carboxylate crystallises with $2C_6H_6$ in large, sulphur-yellow prisms, m. p. 227° .

Methyl phenylindoneacetate, $C_{18}H_{14}O_3$, forms golden-yellow needles, m. p. 108.5° . W. H. G.

Ketens. XIII. Action of Diphenylketen on Carbonyl Derivatives. HERMANN STAUDINGER [and, in part, with J. BECHWITZ] (*Ber.*, 1909, 42, 4249—4262. Compare *Abstr.*, 1908, i, 246, 318, 416, 411, 602).—Experiments have been made by heating diphenylketen in the form of its solid quinoline derivative with equivalent quantities of various ketones at 130° for 1.5 hours, and determining the velocity of reaction by the amount of carbon dioxide eliminated. The reaction proceeds in two stages: the first consisting in the formation of the β -lactone: $CR_2 \cdot O + CPh_2 \cdot CO \rightarrow \begin{smallmatrix} CR_2 \cdot O \\ | \\ CPh_2 \cdot CO \end{smallmatrix}$, and the second in the decomposition of the lactone into carbon dioxide and an olefine derivative: $\begin{smallmatrix} CR_2 \cdot O \\ | \\ CPh_2 \cdot CO \end{smallmatrix} \rightarrow CO_2 + CR_2 \cdot CPh_2$.

It is assumed that the second reaction proceeds with an infinitely greater velocity than the first. The following results have been obtained with the ketones, the formulæ of which are given: $R \cdot CO \cdot CH \cdot CHPh$, 82.3; $R \cdot CO \cdot CN$, 76.3; $R \cdot COH$, 65.9; $R \cdot COPh$, 42.5; $R \cdot COMe$, 32.8; $R \cdot COCl$, 5.5; $R \cdot CO \cdot O \cdot CO \cdot CH \cdot CHPh$, 5.3; $R \cdot CO \cdot OEt$, 5.4; $R \cdot CO \cdot NPh$, 0.0; $R \cdot CO \cdot CH \cdot CH \cdot CH \cdot CHPh$, 85.7; $R \cdot COPh$, 55.6; $R \cdot COMe$, 20.7, where $R = CH \cdot CHPh$, $R' = CH \cdot CH \cdot CH \cdot CHPh$, and the numbers give the percentage amount of the ketone which enters into the reaction. The influence of a double linking on the reactivity of the ketone is not marked, but the results indicate that the reactivity of a ketone with diphenylketen is least when an NR_2 or OR group is attached to the carbonyl, that is, carboxylic derivatives. The carbonyl group, on the other hand, is much more reactive when attached to H, Me, or Ph, and is most reactive when unsaturated groups, for example, cyano and cinnamyl, are present. The results are probably explicable if the state of saturation of the carbonyl group is taken into account in the different compounds.

$\beta\beta$ -Diphenyl- α -styrylacrylonitrile, $CHPh \cdot CH \cdot C(CN) \cdot CPh_2$, obtained

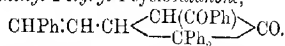
from diphenylketen-quinoline and cinnamoylformonitrile, crystallises in golden-yellow plates, m. p. 157—159°. It is not hydrolysed when boiled with acids or alkalis, but reacts with a chloroform solution of bromine, yielding the *dibromide*, $C_{28}H_{17}NBr_2$, m. p. 143—144°.

Cinnamaldehyde and diphenylketen-quinoline yield *aaδ-triphenylbutadiene*, $CHPh:CH:CH:CPh_3$, which crystallises in colourless needles, m. p. 101·5—102°. With bromine it yields a *bromo-derivative*, $C_{22}H_{17}Br$, in the form of colourless crystals, m. p. 146—148°.

Benzylideneacetophenone and diphenylketen-quinoline yield *aaβδ-tetraphenylbutadiene*, $CHPh:CH:CPh:CPh_3$, and *3-benzoyl-1:1:2-triphenyl-4-cyclobutanone*, $COPh:CH<\begin{smallmatrix} CHPh \\ CO \end{smallmatrix}>CPh_3$, which can be separated

by means of ether, in which the hydrocarbon is somewhat more readily soluble. The ketone crystallises in colourless plates, m. p. 190°. It does not combine with bromine, is stable towards oxidising agents, but reacts with alkalis, yielding diphenylacetic acid. Its *dioxime* has m. p. 191—192°. The tetraphenylbutadiene crystallises in colourless, compact prisms, m. p. 146—148°. It yields a *dibromide*, $C_{28}H_{20}Br_2$, in the form of yellow crystals, m. p. 144—145°, and when oxidised in acetone solution with potassium permanganate or dichromate, yields benzaldehyde and *triphenylacetaldehyde*, $CPh_3:CPh:CHO$, colourless needles, m. p. 175°.

Cinnamylideneacetophenone and diphenylketen-quinoline yield *aaβγ-tetraphenylhexa-Δ⁴,γ-triene*, $CHPh:CH:CH:CH:CPh:CPh_3$, and *3-benzoyl-1:1-diphenyl-2-styryl-4-cyclobutanone*,



The ketone crystallises in colourless needles, m. p. 120—122°, and reacts with bromine, yielding the *bromo-derivative*, $C_{31}H_{23}O_2Br$, m. p. 148—149°. The hexatriene crystallises in yellow prisms, m. p. 158—160°, and yields a *tetrabromide*, $C_{30}H_{24}Br_4$, m. p. 148—150°.

In the combination of the above compounds with bromine, one double linking always remains intact, and this is supposed to be the linking in the $>C:CPh_3$ group. Definite products could not be isolated by heating diphenylketen-quinoline with either benzylideneacetone or cinnamylideneacetone, nor yet with methyl cinnamate or cinnamodiphenylamide.

J. J. S.

Phenylhydrazones of 2-Acetyl-1-naphthol [1-Hydroxy-β-naphthyl Methyl Ketone]: Alkali-insoluble Naphthols. HENRY A. TORREY and C. M. BREWSTER (*J. Amer. Chem. Soc.*, 1909, 31, 1322—1325).—It has been shown by Torrey and Kipper (Abstr., 1908, i, 461) that the phenylhydrazones of certain hydroxyacetophenones are insoluble in aqueous alkali hydroxides, and it is stated that this insolubility is due to the combined influence of the side-chain containing the phenylhydrazine residue in the ortho-position to the hydroxyl group and of another group in the ring, such as the methoxy-group. In the present paper an account is given of the phenylhydrazones of 1-hydroxy-β-naphthyl methyl ketone and its bromo-derivative. These compounds are also insoluble in aqueous

alkali hydroxides, the insolubility in this case being due to the joint effect of the $\cdot\text{CMe:N}\cdot\text{NHPh}$ group in the ortho-position to the hydroxyl group and of the hydrocarbon residue, $\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot$. The hydrazones are very stable, and can be boiled with aqueous alkali hydroxide without undergoing any change. The presence of a bromine atom in the naphthalene ring or in the phenyl group does not affect the insolubility.

4(1)-*Bromo-1-hydroxy- β -naphthyl methyl ketone*, $\text{OH}\cdot\text{C}_{10}\text{H}_7\cdot\text{Br}\cdot\text{COMe}$, m. p. 126—127°, obtained by the action of bromine on an alcoholic solution of the ketone, forms yellowish-green crystals, and condenses with benzaldehyde with production of the *benzylidene* derivative, $\text{OH}\cdot\text{C}_{10}\text{H}_7\cdot\text{Br}\cdot\text{CO}\cdot\text{CH}\cdot\text{CHPh}$, m. p. 176—177°, which forms orange-red crystals. The *phenylhydrazone*, $\text{OH}\cdot\text{C}_{10}\text{H}_7\cdot\text{CMe:N}\cdot\text{NHPh}$, m. p. 136—137°, forms white needles. The *p-bromophenylhydrazone*, m. p. 185—186°, forms silvery-white plates, and the *m-nitrophenylhydrazone*, m. p. 232—233° (decomp.), deep red, compact needles.

The *phenylhydrazones* of the bromo-derivative crystallises in pale yellow needles, and decomposes at 159°. The *p-bromophenylhydrazone*, m. p. 160° (decomp.), forms colourless crystals, and the *m-nitrophenylhydrazone*, m. p. 201—204° (decomp.), deep, orange crystals.

E. G.

Two Isomeric *cyclo*Hexane β -Diketones. GEORGES LESER (*Compt. rend.*, 1909, 149, 1080—1081).—When ethyl acetate is condensed with 1:1-dimethyl-3-*cyclo*hexanone (Abstr., 1899, i, 743), 4-*acetyl*-1:1-dimethyl-3-*cyclo*hexanone, b. p. 111—112°/13 mm., m. p. 28—29°, is formed. It yields a *semicarbazone*, m. p. 171°, has all the properties of a β -diketone, and does not react with magnesium methyl iodide.

The isomeric substance, 2-*acetyl*-1:1-dimethyl-3-*cyclo*hexanone (*loc. cit.*), is soluble in alkalis, does not form a copper derivative, and reacts with magnesium methyl iodide, forming 2-*acetyl*-1:1:3-trimethyl-*cyclo*hexan-3-ol, $\text{CH}_2\langle\begin{smallmatrix} \text{CH}_2 & \text{CH}_2 \\ \text{CMe}(\text{OH}) & \text{CHAc} \end{smallmatrix}\rangle\text{CMe}_2$, m. p. 88—89°, b. p. 232°/750 mm., which crystallises in prismatic needles. On boiling with 20% sulphuric acid, it furnishes the corresponding *dimethyltetrahydroacetophenone*, b. p. 207—208°/745 mm., D_{20}^{25} 0.935, n_D^{20} 1.4776, which has a strong odour of peppermint. On oxidation with permanganate, this furnishes an acid, $\text{C}_8\text{H}_{14}\text{O}_4$, m. p. 86°. T. A. H.

Quinhydrones from Chloranil and Aromatic Hydrocarbons. HERMANN HAAKH (*Ber.*, 1909, 42, 4594—4596. Compare Schlenk, Abstr., 1909, i, 807).—Tetrachloro-*p*-benzoquinone forms intensely coloured *quinhydrones* with stilbene and naphthalene, which are stable at about 100°, but dissociate into their components at the ordinary temperature; the violet *quinhydrones* derived from acenaphthene and acenaphthylene are stable at the ordinary temperature. Interesting is the fact that solutions of chloranil in benzene and xylene are faintly orange and yellowish-red respectively, indicating in the second case partial quinhydrone formation. W. H. G.

Preparation of Halogenated Anthraquinones. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 214714).—Halogenated anthraquinonesulphonic acids were formerly obtained by treating the anthraquinonesulphonic acids in concentrated or fuming sulphuric acid with halogen or halogenating substances. It has now been found that in these acids the sulphonic group is replaced by halogen when this reaction occurs in the presence of water.

A *trichloroanthraquinone* (probably 1:3:4-) is obtained by the action of potassium chlorate and hydrochloric acid on an aqueous solution of sodium 1:4-dichloroanthraquinone- β -sulphonate. It forms yellow needles, m. p. 237°.

1:4-Dichloroanthraquinone- α -sulphonic acid gives a *trichloroanthraquinone*, melting at 253–254°. A *dichlorobromoanthraquinone*, m. p. 233°, is produced by the action of bromine and water at 190° on sodium 1:4-dichloroanthraquinone- β -sulphonate. F. M. G. M.

Preparation of Halogenated Nitroanthraquinones. FARBEN-FABRIKEN VORM. FRIEDRICH BAYER & Co. (D.R.-P. 214150).—The nitroanthraquinonesulphonic acids, like the anthraquinonesulphonic acids, yield halogenated derivatives when treated with aqueous chlorine, the sulphonic group being eliminated in each case.

1-*Chloro-5-nitroanthraquinone* is prepared from sodium 1:5-nitroanthraquinonesulphonate by treatment with sodium chlorate and hydrochloric acid; it forms pale yellow needles. 1:6-, 1:7-, and 1:8-*Chloronitroanthraquinones* were similarly obtained, and the colours of their solutions in various solvents are tabulated in the patent.

F. M. G. M.

[Preparation of Thioglycine Derivatives of Anthraquinone.] FARBENFABRIKEN VORM. FRIEDRICH BAYER & Co. (D.R.-P. 213960. Compare Abstr., 1909, i, 496, 941).—The action of the previously-described thiolanthraquinones on chloroacetylaminanthraquinones leads to the formation of anthraquinonethioglycines having the general formula (A = anthraquinone) $A \cdot S \cdot CH_2 \cdot CO \cdot NH \cdot A$.

The following components and their condensation products are described in the patents:

Chloroacetyl-1-aminoanthraquinone, greenish-yellow needles, and its condensation products with α - and β -thiolanthraquinones.

Chloroacetyl-1-amino-4-hydroxyanthraquinone, orange-red needles, and the products of its condensation with α -thiolanthraquinone and with 1:5-dithiolanthraquinone.

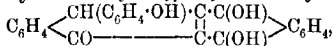
Chloroacetyl-1:4-diaminoanthraquinone, yellowish-brown prisms, and its compound with α -thiolanthraquinone.

Chloroacetyl-1:5-diamino-4:8-dihydroxyanthraquinone, and its condensation product with α -thiolanthraquinone. F. M. G. M.

The Naphthacene Series. III. HUGO VOSWINCKEL and FRITZ DE WEERTH (*Ber.*, 1909, 42, 4648–4650. Compare Abstr., 1906, i, 99; 1909, i, 166).—When naphthacenediquinone, acetic acid, and an excess

of sulphuric acid are heated to a higher temperature than is required for the preparation of 6:11-dihydroxy-6-acetoxy-11-*p*-hydroxyphenyl-dihydronaphthacenequinone, the chief product is 5:12-dihydroxy-11-phenonaphthacenequinone (annexed formula), which crystallises in dark red, pointed prisms, soluble in dilute sodium hydroxide or in concentrated sulphuric acid to red solutions. The diacetyl derivative, $C_{24}H_{12}O_4Ac_2$, has m. p. 264° . The same quinone is formed when the primary condensation product (dihydroxyacetoxy-hydroxy-phenyldihydronaphthacenequinone) is heated with acetic and sulphuric acids; the reduction then proceeds at the expense of part of the quinone, and the product $C_{24}H_{16}O_5$, m. p. 174° (Abstr., 1909, i, 167) is also obtained.

5:12-Dihydroxy-6-keto-11-hydroxyphenyl-6:11-dihydronaphthacene,



obtained by reducing the phenodihydroxynaphthacenequinone with an alkaline solution of sodium hyposulphite, separates as an orange-coloured, crystalline powder, m. p. 225° . The triacetate, $C_{24}H_{12}O_4Ac_3$, forms a pale yellow, crystalline powder, m. p. $206-210^\circ$. When the quinone is reduced with zinc dust and glacial acetic acid, a product, $C_{24}H_{16}O_3$, is obtained as a pale yellow, crystalline powder with no definite m. p. Its acetyl derivative, $C_{26}H_{18}O_4$, has m. p. 171° .

J. J. S.

Stereo- and Structural Isomerides obtained by the Introduction of Acyl Radicles into β -Hydroxylamines. I. GUIDO CUSMANO (*Gazzetta*, 1909, 39, ii, 336-346).—The author describes observations on the action of acyl chlorides on β -hydroxylamines, and shows that this reaction affords a means of obtaining substituted hydroxy-iminic acids.

The compound described by Beckmann and Fleissner (Abstr., 1891, 936) as pulegonehydroxylamine benzoate, m. p. $137-138^\circ$, which may be prepared by the action of benzoyl chloride on pulegonehydroxylamine in ether, is, in reality, anti-menthonylbenzhydroximic acid, $Ph \cdot C \cdot O \cdot C_{10}H_{17}O$, $[\alpha]_D^{20} - 20.14^\circ$ (in alcohol); in freezing acetic acid it has the normal molecular weight, and when treated with sodium ethoxide, it yields sodium benzhydroxamate and pulegone.

syn-Menthonylbenzhydroximic acid, $Ph \cdot C \cdot O \cdot C_{10}H_{17}O$, prepared by

the action of concentrated hydrochloric acid on the anti-compound, or by varying the conditions under which benzoyl chloride and pulegonehydroxylamine react, has m. p. 182° , $[\alpha]_D^{20} - 42.44^\circ$ (in methyl alcohol), and exhibits normal cryoscopic behaviour in acetic acid. Its hydrochloride, m. p. 58° (decomp.), is converted at 100° into an oil, which, with sodium carbonate, yields benzhydroxamic and benzoic

acids and a substance, m. p. 84°, soluble in hydrochloric acid with formation of *syn*-menthonylbenzhydroximic acid.

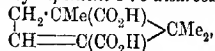
The *menthonyl ether of benzhydroxamic acid*, $\text{Ph} \cdot \overset{\text{N}}{\underset{\text{O}}{\text{C}}} \cdot \text{OH}$
 $\text{N} \cdot \text{OC}_{10}\text{H}_{17}\text{O}'$
 obtained, together with *syn*-menthonylbenzhydroximic acid, by the action of gaseous hydrogen chloride on the *anti*-acid suspended in ether, forms plates, m. p. 96°, and may be converted into *syn*-menthonylbenzhydroximic acid by the action of hydrochloric acid.

T. H. P.

Syntheses in the Camphor and Terpene Series. II. Complete Synthesis of Camphoric Acid and Camphor. GUSTAV KOMPPA (*Annalen*, 1909, 370, 209—233. Compare Abstr., 1909, i, 726).—The present communication contains a detailed account of the synthesis of camphoric acid from *apocamphoric acid*, thereby establishing the validity of Bredt's camphor formula.

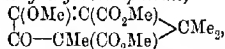
When *diketapocamphoric acid* (1 mol.) is treated with methyl iodide (2 mols.) and sodium methoxide (2 mols.) in methyl-alcoholic solution, it yields a mixture of methyl diketocamphorate and methyl-ketomethoxydehydrocamphorate, which is resolved by treatment with an aqueous solution of sodium carbonate, in which the first named is soluble. *Methyl diketocamphorate*, $\begin{matrix} \text{CO} \cdot \text{CMe}(\text{CO}_2\text{Me}) \\ \text{CO} \cdot \text{CH}(\text{CO}_2\text{Me}) \end{matrix} > \text{CMe}_2$, crystallises in stout plates, m. p. 85—88°; the *copper salt*, $\text{C}_{24}\text{H}_{30}\text{O}_{12}\text{Cu}$, crystallises in stellate groups of bluish-green prisms; the acid is reduced in aqueous solution by sodium amalgam, yielding *4:5-dihydroxycamphoric acid*, obtained as a viscid, yellow syrup; the *silver*, $\text{C}_{10}\text{H}_{14}\text{O}_6\text{Ag}$, and *barium* ($1\text{H}_2\text{O}$) salts are amorphous, white powders.

2:2:3-Trimethyl-Δ²-cyclopentene-1:3-dicarboxylic acid,



is obtained by reducing *4:5-dihydroxycamphoric acid* with hydriodic acid and red phosphorus, also by hydrolysing the ester resulting from the action of diethylaniline on ethyl *α*-bromocamphorate; it crystallises in small, colourless, monoclinic prisms, m. p. 221—223°, and is converted by a solution of hydrogen bromide in glacial acetic acid at 120—125° under pressure into *β*-bromocamphoric acid, obtained as an oil, which, when acted on by zinc dust and glacial acetic acid, yields a mixture of camphoric and *isocamphoric acids*. The *semi-amide* of *γ*-camphoric acid, $\text{C}_{16}\text{H}_{21}\text{O}_3\text{N}$, prepared by the action of aniline on *γ*-camphoric acid in alcoholic solution, crystallises in small, rhombohedra or long needles, m. p. 214.5°—215.5° (corr.).

Methyl 4-keto-5-methoxydehydrocamphorate,



is an ether-like oil, b. p. 156—157°/8 mm., D_{20}^{25} 1.188, n_D^{20} 1.49212, which, when reduced with sodium amalgam and methyl alcohol, yields the corresponding hydroxy-acid, from which dehydrocamphoric acid is obtained by treatment with hydriodic acid and red phosphorus.

W. H. G.

Condensation Products from Camphor. MARCEL GUERRET (*Compt. rend.*, 1909, 149, 931—933.* Compare Abstr., 1909, i, 310).—The formation of neutral, oily products when the mixture resulting from the action of sodium on a solution of camphor in toluene is heated at 280° has been observed by Montgolfier (Abstr., 1878, 891), who supposed them to have the composition $(C_{10}H_{16})_n$. The oil has now been distilled, and from the fraction b. p. 326—335° two condensation products isolated.

(i) *Bornylencamphor*, $C_8H_{14} \begin{smallmatrix} \diagup & C=C & \diagdown \\ & CO & CH_2 \end{smallmatrix} C_8H_{14}$ occurs as colourless needles, m. p. 93°, $[\alpha]_D + 69.2^\circ$ in alcohol. It unites with hydrogen bromide, forming a compound, $C_{20}H_{31}OBr$, m. p. 202—203°. Bromine attacks it, liberating hydrogen bromide and yielding *bromobornylencamphor*, $C_{20}H_{29}OBr$, m. p. 101°. Warm fuming nitric acid converts bornylencamphor into a nitro-derivative, $C_{20}H_{29}O \cdot NO_2$, which crystallises in colourless, rhombic tablets, m. p. 204°, and forms a sodium salt, $C_{20}H_{28}ONa \cdot NO_2 \cdot 3H_2O$, occurring as pearly leaflets.

(ii) *Bornylcamphor*, $C_8H_{14} \begin{smallmatrix} \diagup & CH \cdot CH & \diagdown \\ & CO & CH_2 \end{smallmatrix} C_8H_{14}$, crystallises in needles, m. p. 77.5°, and can also be prepared by the reduction of benzylidene-camphor by sodium amalgam in acid alcoholic solution.

W. O. W.

Composition of Oil of Turpentine. EUGÈNE DARMOIS (*Compt. rend.*, 1909, 149, 730—733. Compare Abstr., 1908, ii, 747).—A further application of measurements of rotatory dispersion to the determination of the composition of optically active hydrocarbons. Dextrorotatory turpentine contains *d*-pinene, together with a hydrocarbon showing feebly levorotatory dispersive power and having $[\alpha]_D - 21.7^\circ$. The latter appears also to be present in French lavo-oils, and may be identical with nopinene. The b. p. of the oil from *Pinus halepensis* remains constant at 155° for 90% of the product; the distillate shows strong dispersion, and has $[\alpha]_D + 82.8^\circ$, m. p. -50°.

By the application of Biot's law of mixtures as previously indicated, the proportion of pinene in French lavo-oils and in Algerian dextro-oils is found to be 62%.

W. O. W.

Hydrogenation in the Terpene Series. G. VAYON (*Compt. rend.*, 1909, 149, 997—999).—Pinene rapidly absorbs hydrogen in presence of platinum-black. In this way the α -pinene (Algerian) prepared by Darmois (preceding abstract) has furnished, in quantitative yield, a hydrocarbon, $C_{10}H_{18}$, b. p. 166°/755 mm., $[\alpha]_D + 22.7^\circ$, $D_4^{20} 0.861$, solidifying at about -45°. It differs from the hydrocarbon described by Sabatier and Senderens (Abstr., 1901, i, 459) in remaining unaltered on exposure to air. Under the same conditions, French *l*-pinene yields the same compound, but having $[\alpha]_D - 21.3^\circ$; α - and β -pinene therefore appear to yield the same substance on hydrogenation.

Camphene forms a hydrocarbon, $C_{10}H_{18}$, m. p. about 87°, which is not identical with that obtained by Sabatier and Senderens (*loc. cit.*)

* and *J. Pharm. Chim.*, 1910, [vii], 1, 5—10.

by the action of water on the magnesium derivative of camphene hydrochloride.

Limonene, $[\alpha]_D +121.3^\circ$, combines with $4H$, giving an inactive hydrocarbon, b. p. 169° , D_{15}^{20} 0.803. Maleic, fumaric, cinnamic, and ercnic acids have been hydrogenated in the same way. W. O. W.

[α -Terpinene.] KARL AUWERS. (*Ber.*, 1909, 42, 4427—4429. Compare Abstr., 1909, i, 592).—Polemical. A reply to Semmler (Abstr., 1909, i, 942). R. V. S.

Constituents of Ethereal Oils. I. Terpinolene. II. Terpinene. FRIEDRICH W. SEMMLER and ENDRE SCHLOSSBERGER (*Ber.*, 1909, 42, 4644—4647).—I. Pure terpinolene is best prepared by the action of zinc dust on an ethereal-alcoholic solution of the pure tetrabromide, m. p. 115 — 116° . When acetic acid is used, the product always contains appreciable amounts of terpinene. Pure terpinolene has b. p. 67 — $68^\circ/10$ mm., D_{20}^{20} 0.854, and n_D^{20} 1.484.

II. Terpinene. Polemical (compare Auwers, preceding abstract). J. J. S.

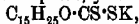
Cryptomeria Japonica Oil. H. KIMURA (*Ber. Dent. pharm. Ges.*, 1909, 19, 369—387).—The oil distilled from the wood of this tree is shown to consist to the extent of 60% of the sesquiterpenes, *L*-cadinene and suginene, the residue being a sesquiterpene alcohol, cryptomeriol (compare Kimoto, *Chem. Centr.*, 1902, ii, 382; Keimatsu, *Pharm. J.*, 1905, 189).

On steam distillation the wood yields 1.5% of a yellow oil, which darkens and thickens on standing. The re-distilled oil has D 0.9590,

sesquiterpene, which has received into its composition of treatment with hydrogen chloride, which furnished a solid and a liquid dihydrochloride. The former had m. p. 117 — 118° and $[\alpha]_D -37^\circ 1'$ in chloroform, and proved to be identical with *L*-cadinene dihydrochloride from cade oil. The liquid hydrochloride on treatment with sodium acetate and acetic acid regenerated a new sesquiterpene, *suginene*, D 0.918, $[\alpha]_D -10^\circ 34'$, which yields a liquid dihydrobromide, b. p. 140 — $150^\circ/16$ mm., D 0.988, $[\alpha]_D -11^\circ 15'$. The sesquiterpene regenerated from this had D 0.921 and $[\alpha]_D +14^\circ 43'$, whilst that regenerated from the liquid dihydrobromide had D 0.911 and $[\alpha]_D -24^\circ 21'$. No crystalline derivatives of *suginene* could be obtained, but it appears to be oxidised to an alcohol by treatment with bromine water.

The alcoholic portion of the oil was isolated by treatment with potassium wire, the sesquiterpene portion being then removed by distillation under reduced pressure. The potassium derivative was freed from excess of potassium and other impurities by solution in ether. The potassium derivative, on treatment with water, furnished cryptomeriol, $C_{15}H_{25}OH$, b. p. 162 — $163^\circ/10$ mm., D 0.964,

$[\alpha]_D - 37.5$, a thick, colourless oil. The potassium derivative of this, when treated with carbon disulphide, yielded a *zanthic* ester,



which on addition of water did not regenerate the original alcohol, but colourless, crystalline *isocryptomeriol*, $C_{15}H_{26}O$, m. p. $135-136^\circ$, and a new liquid *alcohol*, $[\alpha]_D - 3.25'$. On treatment with formic acid, *cryptomeriol* yielded a *sesquiterpene*, D 0.918, b. p. $143-144^\circ/13$ mm., $[\alpha]_D - 1.5'$, and with phosphoric oxide, a second *sesquiterpene*, D 0.917, $[\alpha]_D + 56.26'$, which was also prepared from the first *sesquiterpene* by the action of phosphoric oxide. Both gave liquid products with gaseous halogen acids.

Cadinene cannot be regenerated unchanged from its compounds with the halogen acids.

T. A. H.

Volatile Oil of Rhus Cotinus ("Young Fustic"). GUSTAVE PERRIER and A. FOUCHET (*Bull. Soc. chim.*, 1909, [iv], 5, 1074-1075).—The leaves and twigs on steam distillation yield 0.1% of a colourless, volatile oil with an odour somewhat recalling that of oil of turpentine. The oil has $D_{15} 0.875$, $n_D 1.4693$, $[\alpha]_D + 13^\circ$, is completely soluble in alcohol of 94° , is acid to litmus, contains free alcohols, and gives the aldehyde reaction with Schiff's reagent.

T. A. H.

Catalytic Oxidation of Guaiacum Resin by Copper. HECTOR A. COLWELL (*J. Physiol.*, 1909, 39, 358-360).—Both metallic copper and its salts have a catalytic oxidising action on guaiacum, which is remarkable among the other metals examined for its intensity.

W. D. H.

Preparation of Indican. HENRI TER MEULEN (*Rec. trav. chim.*, 1909, 28, 339-341).—In a previous paper (*Abstr.*, 1900, i, 404) the author has shown with Hoogewerff, that indican may be prepared conveniently from plants containing it, by extraction with boiling water, but Perkin and Bloxam have stated recently (*Trans.*, 1907, 91, 1715) that in their experience extraction with water gives a smaller yield of indican than is obtained with acetone as a solvent.

The author has repeated the previous work with material supplied to him by Perkin and Bloxam, and finds that, using his modified process (*Rec. trav. chim.*, 1905, 24, 468), he obtains 2.7% of indican as compared with 3.166% found by Perkin and Bloxam, so that extraction with hot water does not necessarily involve any material loss of glucoside.

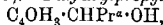
T. A. H.

Active Principle of a Benin Spear Poison. PATRICK P. LAIDLAW (*J. Physiol.*, 1909, 39, 354-357).—The supply of poison was obtained from two spear heads from Benin. Although attempts to prepare a pure crystalline toxic substance failed, owing to impurities, there is no doubt that the poison is a glucoside which has the solubilities and physiological properties of strophanthin; it also gives the characteristic colour reaction of that substance.

W. D. H.

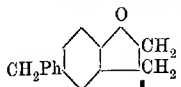
Discovery of the Optical Activity of Tannin. EDMUND O. VON LIPPMANN (*Ber.*, 1909, 42, 4678—4679. Compare Rosenheim, *Abstr.*, 1909, i, 599).—C. Scheibler (*Zeitsch. Zuckerind.*, 1866, 18, 33) appears to have been the first to draw attention to the optical activity shown by certain specimens of tannin. J. J. S.

Furfurylpropylcarbinol. Mlle. EUGÉNIE JOLKVER (*Rec. trav. chim.*, 1909, 28, 439—443).—*Furfurylpropylcarbinol*,



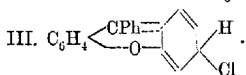
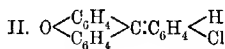
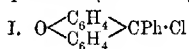
b. p. 92—93°/12 mm. or 195—198°/760 mm., prepared by Grignard's method (*Abstr.*, 1901, i, 680) from magnesium propyl bromide and furfuraldehyde, is a colourless liquid, which becomes yellow on exposure to light. The corresponding *chloride* has b. p. 90—91°/6 mm. or 94—95°/10 mm., and the *acetate*, b. p. 96—97°/22 mm. or 106°/28 mm., is a colourless, mobile liquid of pleasant odour. T. A. H.

4-Benzylcumaran. CHARLES MARSCHALK (*Ber.*, 1909, 42, 4485—4487). — 4-Benzylcumaran (annexed



formula), prepared by the reduction of 4-benzoylcumaran (compare *Abstr.*, 1907, i, 950) by means of sodium and alcohol, forms white crystals, m. p. 61°, and dissolves in concentrated sulphuric acid, giving a yellow solution, which becomes green on addition of ferric chloride. This compound is presumably the mother substance of the catechin group. T. II. P.

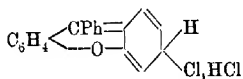
Triphenylmethyl. XVIII. Quinocarbonium Salts. MOSES GOMBERG and LEE H. CONE (*Annalen*, 1909, 370, 142—208. Compare *Abstr.*, 1907, i, 504; 1909, i, 141).—A complete parallelism is shown to exist between the salts of triphenylcarbinol and its derivatives and the salts of xanthenol and analogous substances, from which the conclusion is drawn that the compounds which have been regarded previously as carboxonium salts (compare Kehrman, *Abstr.*, 1900, i, 61; Werner, *Abstr.*, 1902, i, 50) are really carbonium salts, and, like triphenylcarbinol chloride, capable of existing in a benzenoid (I) and a quinonoid (II and III) form:



When hydrogen chloride is passed into a solution of xanthenol in an indifferent solvent, a yellow precipitate is obtained, which is a hydrochloride of xanthenol chloride (quinoxanthenol chloride hydrochloride); the mol. of hydrogen chloride may be removed by suitable treatment, leaving a colourless chloride. The normal, colourless xanthenol chlorides are very similar in their chemical behaviour to triphenylcarbinol chloride. They give yellow solutions when dissolved in liquid sulphur dioxide, showing that they exist in two tautomeric

forms, a further proof of which is shown by the behaviour of phenyl-*p*-bromoxanthanol bromide, which when treated with silver chloride yields phenyl-*p*-chloroxanthanol chloride.

The formation of coloured derivatives is induced, not only by sulphur dioxide and hydrogen chloride, but also by metallic halides, sulphuric acid, and perchloric acid. The last-mentioned acid forms stable, crystalline salts, not only with xanthanol derivatives, but also with those of triphenylmethane, which latter do not contain oxygen. The colour of these salts cannot be due, therefore, to the formation of oxonium salts.

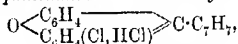


Phenylxanthanol (compare Bünzly and Decker, Abstr., 1904, i, 912) when treated in chloroform with a solution of acetyl chloride and subsequently with hydrogen chloride yields *phenylquinoxanthanol chloride hydrochloride* (annexed formula), crystallising in glistening, reddish-orange prisms; the *chloride*, $\text{O}(\text{C}_6\text{H}_5)_2\text{CPhCl}$, is obtained by passing air through a solution of the hydrochloride just described at about 50–60° in the complete absence of water; it crystallises in colourless prisms, m. p. 105–106°. A solution of the chloride in benzene (1) when heated under pressure with silver yields an *unsaturated* compound, which, in analogy to triphenylmethyl, absorbs oxygen quite readily, yielding *phenylxanthanol peroxide*, $[\text{O}(\text{C}_6\text{H}_5)_2\text{CPh}]_2\text{O}_2$, transparent, colourless, glistening leaflets, m. p. 219° (decomp.), and (2) when treated with magnesium benzyl chloride yields $\alpha\beta$ -*diphenyl- α -xanthylethane*, $\text{O}(\text{C}_6\text{H}_5)_2\text{CPh}\cdot\text{CH}_2\text{Ph}$, colourless, rhombic prisms, m. p. 169°. The following additive compounds of the chloride have been prepared: *ferrichloride*, $\text{C}_{19}\text{H}_{13}\text{OCl}_2\text{FeCl}_3$, brownish-red spangles, sinters at 167°, m. p. 170°; *mercurichloride*,

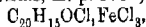
$\text{C}_{19}\text{H}_{13}\text{OCl}_2\text{HgCl}_2$, white powder, sinters at 230°, m. p. 248–250° (decomp.); *perbromide*, $\text{C}_{19}\text{H}_{13}\text{OClBr}_2$, unstable, orange-yellow powder, sinters at 146°, m. p. 150° (decomp.); *periodide*, $\text{C}_{19}\text{H}_{13}\text{OClI}_2$, brownish-red, crystalline powder; *perchloride*, $\text{C}_{19}\text{H}_{13}\text{OCl}_3$, orange-red needles. *Phenylxanthanol hydrogen sulphate*, $\text{C}_{19}\text{H}_{13}\text{O}\cdot\text{SO}_3\text{H}$, forms stellate aggregates of orange crystals, m. p. 175°; the *perchlorate*, $\text{C}_{19}\text{H}_{13}\text{O}\cdot\text{ClO}_4$, obtained by the action of silver perchlorate on the chloride or directly from perchloric acid and phenylxanthanol, crystallises in golden, transparent prisms, m. p. 281–282°.

The following compounds are obtained by methods similar to those just described.

p-Tolylxanthanol, $\text{O}(\text{C}_6\text{H}_4\text{Me})_2\text{C}(\text{OH})\text{Ph}$, prepared from xanthone and *p*-iodotoluene, crystallises in groups of small, transparent plates, m. p. 150°. *p*-Tolylquinoxanthanol chloride hydrochloride,



is an unstable, brown, crystalline substance. The *chloride*, $\text{O}(\text{C}_6\text{H}_4\text{Me})_2\text{C}(\text{C}_6\text{H}_4\text{Me})\text{Cl}$, crystallises in colourless prisms, m. p. 131°; *ferrichloride*,



yellowish-brown crystals, sinters at 205° , m. p. 211° ; *zinc chloride*, $C_{20}H_{15}OCl, ZnCl_2$, brownish-yellow needles, sinters at 233° , m. p. $240-247^{\circ}$ (decomp.); *perbromide*, $C_{20}H_{15}OCl, Br_2$, amorphous, brownish yellow powder; the *perchlorate*, $C_{20}H_{15}O \cdot ClO_4$, crystallises in yellow needles, m. p. 239° . *p-Tolylxanthanol peroxide*, $C_{40}H_{20}O_4$, forms colourless, glistening prisms, m. p. 212° (decomp.).

Phenylidinaphthoxanthanol, $O \langle \underset{C_{10}H_6}{C_{10}H_5} \rangle CPh \cdot OH$, prepared by oxidising benzylidene- β -dinaphthyl oxide in glacial acetic acid with lead peroxide, has m. p. $265-268^{\circ}$. *Phenylidinaphthoquinoxanthanol chloride hydrochloride*, $C_{27}H_{17}OCl_2$, crystallises in long, dark red, glistening needles, loses hydrogen chloride when heated, becomes white at 230° , m. p. $270-274^{\circ}$. *Phenylidinaphthoxanthanol chloride*, $C_{27}H_{17}OCl$, forms almost colourless crystals, m. p. 274° ; the *ferrichloride*, $C_{27}H_{17}OCl, FeCl_3$, dark red needles; *stannichloride*, $C_{27}H_{17}OCl, SnCl_4$, red crystals, and *zinc chloride*, $C_{27}H_{17}OCl, ZnCl_2$, glistening, red needles, were analysed; the *hydrogen sulphate*, $C_{27}H_{17}O \cdot SO_4H \cdot \frac{1}{2}H_2SO_4$, forms long, red needles, m. p. $145-150^{\circ}$; the *perchlorate*, $C_{27}H_{17}O \cdot ClO_4$, crystallises in scarlet leaflets with a golden shimmer, and does not melt at 280° .

p-Methoxyphenylidinaphthoquinoxanthanol chloride hydrochloride, $C_{28}H_{19}O_2Cl, HCl$, forms dark red, glistening crystals, m. p. 235° (decomp.). *p-Methoxyphenylidinaphthoxanthanol chloride*, $O \langle \underset{C_6H_4}{C_6H_3} \rangle C(C_6H_4 \cdot OMe)Cl$, forms white crystals; the red, crystalline *additive* products with ferric chloride, m. p. $235-237^{\circ}$, stannic chloride, zinc chloride, and iodine were analysed; the *hydrogen sulphate*, $C_{28}H_{19}O_2 \cdot SO_4H \cdot \frac{1}{2}H_2SO_4$, bright red needles, m. p. 145° , and *perchlorate*, $C_{28}H_{19}O_2 \cdot ClO_4$, were analysed.

p-Chlorophenylxanthanol, $O \langle \underset{C_6H_4}{C_6H_3} \rangle C(C_6H_4Cl) \cdot OH$, has m. p. 173° ; the *chloride*, $C_{19}H_{12}OCl_2$, forms colourless, transparent prisms, m. p. about $104-105^{\circ}$, and when treated with alcohol yields *p-chlorophenylxanthanol ethyl ether*, $C_{21}H_{17}O_2Cl$, crystallising in tufts of colourless crystals, m. p. $120-121^{\circ}$; the *additive* compounds of the chloride with ferric chloride, m. p. $209-210^{\circ}$, zinc chloride, and bromine, m. p. 166° (decomp.), were analysed; they are orange-red, crystalline powders. *p-Chlorophenylxanthanol peroxide*, $C_{38}H_{24}O_4Cl_2$, prepared by the action of silver and air on a solution of the chloride in benzene, crystallises with benzene in colourless, glistening prisms, m. p. 213° (decomp.). *p-Chlorophenylquinoxanthanol chloride hydrochloride*,

$C_{19}H_{12}OCl_2, HCl$, forms brownish-yellow needles.

p-Bromophenylxanthanol, $C_{19}H_{12}O_2Br$, crystallises in long, colourless, pointed needles, m. p. 183° ; the *chloride*, $C_{19}H_{12}OBrCl$, forms transparent, colourless prisms, m. p. $118-119^{\circ}$; the *perchlorate*,

$C_{19}H_{12}OBr \cdot ClO_4$, is a crystalline, orange powder, sinters at 295° , m. p. about 310° . *p-Bromophenylquinoxanthanol chloride hydrochloride*, $C_{19}H_{12}OClBr, HCl$, crystallises in yellow needles. *p-Bromophenylxanthanol peroxide*,

$C_{38}H_{24}O_4Br_2$, crystallises in colourless, rhombic plates, m. p. $210-211^{\circ}$ (decomp.).

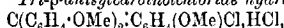
Phenyl-p-chloroxanthanol, $O \langle \underset{C_6H_4}{C_6H_3Cl} \rangle CPh \cdot OH$, prepared from

4-chloroxanthone and magnesium phenyl bromide, crystallises in slender leaflets, m. p. 164° ; the *chloride*, $C_{19}H_{12}OCl_2$, crystallises in rosettes of colourless rods, m. p. 151° . 4-Chloroxanthone was prepared as follows: 2:4-dichloroaniline is converted into 2:4-dichlorobenzonitrile, colourless prisms, m. p. 61° , which when hydrolysed yields 2:4-dichlorobenzoic acid, m. p. 164° ; the latter substance when treated with sodium phenoxide and copper powder yields 4-chloro-2-phenoxybenzoic acid, m. p. 171° , which is converted by warm concentrated sulphuric acid into 4-chloroxanthone, m. p. 130° . The compound, m. p. 171° , described by Ullmann and Wagner is probably an isomeric (compare Abstr., 1907, i, 846). Phenyl-*p*-chloroquinoxanthanol chloride hydrochloride, $C_{19}H_{12}OCl_2 \cdot HCl$, is an extremely unstable, red, crystalline substance.

Phenyl-*p*-bromoxanthanol, $C_{19}H_{12}O_2Br$, prepared by way of 4-bromo-2-phenoxybenzoic acid, $C_{13}H_8O_3Br$, crystallising in rosettes of needles, m. p. 178° , and 4-bromoxanthone, colourless needles, m. p. 126° , is obtained in colourless crystals, m. p. 145° ; the bromide, $C_{19}H_{12}OBr_2$, crystallises in almost colourless needles, m. p. 155° . Phenyl-*p*-bromoxanthanol bromide hydrobromide, $C_{19}H_{12}OBr_2 \cdot HBr$, crystallises in orange-red prisms with a blue reflex.

II. Hydrochlorides and Perchlorates in the Triphenylmethane Series.—

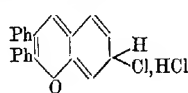
Phenyl-di-*p*-anisylcarbinol chloride combines with hydrogen chloride, forming a *hydrochloride*, $OMe \cdot C_6H_4 \cdot CPh : C_6H_4(OMe)Cl \cdot HCl$, obtained as a dark red oil. Tri-*p*-anisylcarbinolchloride hydrochloride,



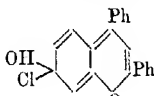
crystallises in dark red needles with a blue reflex (compare Baeyer and Villiger, Abstr., 1903, i, 811).

The *perchlorates* of the following compounds have been prepared and analysed: triphenylcarbinol, $C_{19}H_{15} \cdot ClO_4$, red crystals, m. p. 150° ; diphenyl-*p*-tolylcarbinol, $C_{20}H_{17} \cdot ClO_4$, brown crystals; tri-*p*-tolylcarbinol, $C_{22}H_{21} \cdot ClO_4$, $\frac{1}{2}C_6H_5 \cdot NO_2$, glistening, violet crystals, m. p. 187° ; *p*-chlorotriphenylcarbinol, $C_{19}H_{14}Cl \cdot ClO_4$, compact, red crystals, m. p. $142-144^{\circ}$; *p*-bromotriphenylcarbinol, red crystals with a blue reflex, m. p. 151° ; tri-*p*-chlorotriphenylcarbinol, small, brownish-red plates with a violet reflex, m. p. $172-174^{\circ}$; tri-*p*-bromotriphenylcarbinol, $C_{19}H_{13}Br_3 \cdot ClO_4$, dark brownish-red crystals, m. p. $174-175^{\circ}$; diphenyl-*p*-anisylcarbinol, $C_{20}H_{17}O \cdot ClO_4$, red needles, m. p. 192° ; phenyl-di-*p*-anisylcarbinol, dark red needles, m. p. $112-113^{\circ}$; tri-*p*-anisylcarbinol, $C_{22}H_{21}O_3 \cdot ClO_4$, dark purple needles, m. p. 195° .

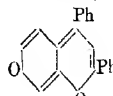
III. *Derivatives of Benzo- γ -pyrone*.—The pyranols are regarded as being strictly analogous to the xanthenols, the coloured pyranol salts being quinocarbonium salts (compare Decker, Abstr., 1907, i, 1064).



(I.)



(II.)



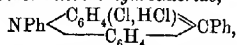
(III.)

2:3-Diphenylbenzopyranol chloride hydrochloride (formula I) crystallises in long, yellow needles.

[With O. B. WINTER.]—7-Hydroxy-2:4-diphenylbenzopyranol chloride hydrochloride, $C_{21}H_{16}O_2Cl_2$, forms orange-red crystals; it loses 1HCl when dry air is passed through the solution in chloroform, yielding the orange-yellow quinonoid chloride (formula II); if the solution be heated, another mol. of hydrogen chloride is evolved, with the formation of the quinone (formula III), an amorphous, red powder.

IV. *Acridine Derivatives*.—The salts of the phenylacridols are probably quinocarbonium salts of the same type as the coloured salts of phenylxanthenol.

5:10-Diphenylacridol chloride hydrochloride,



crystallises in golden needles; the chloride, $C_{25}H_{18}NCl$, prepared by the action of acetyl chloride on 5:10-diphenylacridol, crystallises with 1Me·CO₂H and 2C₆H₆ in yellow crystals, and with 2CHCl₃ in yellow plates; it is also obtained by heating the hydrochloride in a vacuum at 150°, and does not melt at about 300°. W. H. G.

3:6-Dimethylfluoran. ENOS FERRARIO and M. NEUMANN (*Bull. Soc. chim.*, 1909, [iv], 5, 1098—1101. Compare Lambrecht, *Abstr.*, 1909, i, 949).—3:6-Dimethylfluoran, m. p. 213.5° (corr.), has been obtained by the action of phthalyl chloride on *m*-cresol, and also in 80% yield by heating phthalic anhydride with *m*-cresol and zinc chloride. The compound is readily esterified by heating with alcoholic hydrogen chloride; on the addition of platinic chloride, the *platini-chloride*, $(C_9H_{16}OCl \cdot CO_2Et)_2PtCl_4$, separates. The *methyl ester*, $C_{21}H_{17}O \cdot CO_2Me$, has m. p. 115—116°.

The addition of bromine to a solution of dimethylfluoran in acetic acid results in the formation of an unstable, red oxonium *tribromide*. A *dibromo-derivative*, m. p. 249—250°, and a *tetrabromo-derivative*, m. p. 306°, have also been obtained. Dimethylfluoran forms a *tetranitro-derivative*, $C_{22}H_{12}O_{11}N_4$, and possibly a *dinitro-derivative*, m. p. 242°. The former decomposes at about 280°, and on reduction yields an amine, the *picrate* of which decomposes at 120—121°. W. O. W.

Preparation of 2:3-Diketodihydro-(1)-thionaphthen Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 213458. Compare *Abstr.*, 1909, i, 950).—2:3-Diketodihydro-1-thionaphthen-3-oxime is prepared by adding sodium nitrite to a cooled solution of 3-oxy-1-thionaphthen in aqueous sodium hydroxide and subsequent acidification with dilute sulphuric acid. It forms yellow, silky prisms, m. p. 168°. The *acetyl derivative*, m. p. 168°, and the *phenylhydrazone*, m. p. 154°, are described.

On hydrolysing the preceding compound with 15% hydrochloric acid and reducing the colourless product with iron filings, it yields 2:3-diketodihydro-1-thionaphthen, the *phenylhydrazone* of which has m. p. 162°, and the *dianilino-derivative*, m. p. 80°.

The higher homologues of the foregoing compounds are similarly prepared, 3-oxy-5-methyl-(1)-thionaphthen yielding 2:3-diketo-5-methyl-

dihydro-(1)-thionaphthen-2-oxime, m. p. 185°, and *5-chloro-3-oxo-(1)-thionaphthen* gives *5-chloro-2:3-diketodihydro-1-thionaphthen-2-oxime*, m. p. 188°. F. M. G. M.

Preparation of Derivatives of 2:3-Diketodihydro-(1)-thionaphthens. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 214781).—Derivatives of 2:3-diketodihydro-(1)-thionaphthen have formerly been obtained by the action of aromatic amines on the dihalogenated derivatives of 3-ketodihydro-(1)-thionaphthen and hydrolysis of the product. It has now been found that nitroso-derivatives of aromatic amines will condense with 3-oxo-(1)-thionaphthen itself, giving rise to a condensation product which, on hydrolysis, furnishes the diketocompound.

3-Oxy-(1)-thionaphthen in alcoholic or dilute alkali solution condenses at 40° with *p*-nitrosodimethylaniline, giving the compound (m. p. 176°), $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{S} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C:N} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$. This product, when hydrolysed with 15% hydrochloric acid, gives 2:3-diketodihydro-(1)-thionaphthen.

p-Nitrosoethylaniline and *p*-nitrosodiphenylamine give similar products, melting at 158° and 193° respectively, which also undergo hydrolysis to furnish the diketone.

3-Oxy-5-methyl-(1)-thionaphthen, when submitted to this series of operations, yields 2:3-diketo-5-methyldihydro-1-thionaphthen, m. p. 143°. F. M. G. M.

Poly-membered Heterocyclic Systems containing Sulphur, and Ring Closure in the Para-Position. WILHELM AUTENRIETH and FRITZ BEUTTEL (*Ber.*, 1909, 42, 4346—4357).—It has been shown recently that dihydric mercaptans readily condense with aldehydes or ketones to form compounds containing six-, seven-, or sixteen-membered heterocyclic systems containing sulphur. The ease with which *o*-xylylene hydrosulphide reacts has suggested the use of the para-isomeride also.

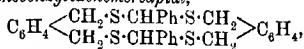
p-Xylylene hydrosulphide, prepared by adding a boiling alcoholic solution of *p*-xylylene bromide to alcoholic potassium hydrosulphide saturated with hydrogen sulphide (compare Kütz, *Abstr.*, 1900, i, 343), is separated by means of dilute aqueous sodium hydroxide from the simultaneously formed *monothyl ether* of *p*-xylylene glycol,



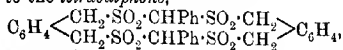
b. p. 250—252°. *p*-Xylylene hydrosulphide condenses, in the presence of hydrogen chloride, with aliphatic aldehydes or ketones to form only amorphous, rather indefinite products, but with aromatic aldehydes beautifully crystalline duplo-compounds are obtained, which are similar to those obtained from pentamethylene hydrosulphide (Autenrieth and Geyer, *Abstr.*, 1909, i, 6). The duplo-compounds contain an eighteen-membered ring, and are very stable; nascent hydrogen does not cause the elimination of hydrogen sulphide or of the mercaptan; oxidising agents do not rupture the ring, and the compounds are stable to boiling alcoholic potassium hydroxide, but

undergo deep-seated changes by treatment with fuming hydrochloric acid at 180°.

Duplo-p-xylylenebenzylidenemercaptal,



m. p. 248—249°, is prepared by passing hydrogen chloride into an ice-cold mixture of equal molecular quantities of benzaldehyde and *p*-xylylene hydrosulphide. It crystallises in silvery leaflets, and has a molecular weight in naphthalene corresponding with its formula. In warm benzene it is oxidised by potassium permanganate and sulphuric acid to the *tetrasulphone*,



which melts above 300°.

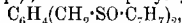
Duplo-p-xylylene-p-tolylidenemercaptal, $\text{C}_{32}\text{H}_{32}\text{S}_4$, m. p. 266°, is prepared in a similar way, and yields a *tetrasulphone*, $\text{C}_{32}\text{H}_{28}\text{O}_8\text{S}_4$, m. p. 280—282° (decomp.). *Duplo-p-xylylene-m-tolylidenemercaptal*,



m. p. 219—220°, is similarly obtained in almost theoretical yield. *Duplo-p-xylylene-p-hydroxybenzylidenemercaptal*, $\text{C}_{30}\text{H}_{28}\text{O}_3\text{S}_4$, m. p. 262—264° (decomp.), is prepared in ethereal solution, and yields a *dibenzoate*, m. p. 233°, by the Schotten-Baumann process.

Duplo-p-xylylene-m-hydroxybenzylidenemercaptal, $\text{C}_{30}\text{H}_{28}\text{O}_3\text{S}_4$, m. p. 251—252° (decomp.), is also prepared in ethereal solution, and forms a *dibenzoate*, m. p. 169°.

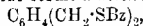
p-Xylylene hydrosulphide forms a *dibenzoate*, m. p. 135°, and a *dibenzyl thioether*, $\text{C}_6\text{H}_4(\text{CH}_2 \cdot \text{S} \cdot \text{C}_6\text{H}_5)_2$, m. p. 65°. The latter in benzene solution is oxidised by potassium permanganate and sulphuric acid mainly to the corresponding *disulphone*, $\text{C}_{22}\text{H}_{22}\text{O}_4\text{S}_2$, m. p. 292—294° (decomp.); the accompanying *disulphoxide*,



m. p. 232—233°, is removed by acetone; it is more conveniently prepared by the addition of 30% hydrogen peroxide to a cold solution of the *dibenzyl thioether* in glacial acetic acid. C. S.

Poly-membered Heterocyclic Systems containing Sulphur, and Ring Closure in the Meta-Position. WILHELM AUTENRIETH and FRITZ BEUTTEL (*Ber.*, 1909, 42, 4357—4361).—The following compounds are prepared by methods similar to those described in the preceding abstract.

m-Xylylene hydrosulphide forms a *dibenzoyl* derivative,



m. p. 52.5°, and a *dibenzyl thioether*, m. p. 48°. *m*-Xylylenedibenzyl-*disulphone*, $\text{C}_6\text{H}_4(\text{CH}_2 \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_5)_2$, has m. p. 225°.

After many attempts with various aliphatic and aromatic aldehydes and ketones, the authors have succeeded in condensing *m*-xylylene hydrosulphide and acetone in the presence of hydrogen chloride, the crystalline product being the *duplo-m-xylenemercaptal of acetone*, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \cdot \text{S} \cdot \text{CMe}_2 \cdot \text{S} \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{S} \cdot \text{CMe}_2 \cdot \text{S} \cdot \text{CH}_2 \end{array} > \text{C}_6\text{H}_4$, m. p. 254°, which is stable to alcoholic potassium hydroxide, nascent hydrogen, potassium perman-

ganate and sulphuric acid, and hydrogen peroxide; the corresponding tetrasulphone, $C_{42}H_{28}O_8S_4$, melts above 300° , and is insoluble in all known organic solvents. Its molecular weight is assumed, by analogy, to correspond with the preceding formula. C. S.

Crystalline Alkaloid of Calycanthus Glauco. III. *iso*-Calycanthine, Isomeric with Calycanthine. HARRY M. GORDIN (*J. Amer. Chem. Soc.*, 1909, 31, 1305—1312).—In earlier papers (Abstr., 1905, i, 295; 1906, i, 35), calycanthine and its salts have been described.

On extracting the alkaloid from a new quantity of seed, a product was obtained which, although resembling calycanthine in composition and general appearance, differs from it in several important respects, and is therefore termed *isocalycanthine*. Whether the two samples of seed were derived from different species of *Calycanthus* or the difference between the alkaloids was due to a difference in the age of the plants is not at present known.

isoCalycanthine, $C_{11}H_{14}N_{2.2}H_2O$, m. p. $212-214^\circ$, forms crystals of the bisphenoidal class of the orthorhombic system [$a:b:c=1.2557:1:1.3226$], and has $[\alpha]_D^{20}$ $697-97^\circ$; the anhydrous alkaloid has m. p. $235-236^\circ$. The hydrochloride, hydrobromide, hydriodide, platinumchloride, aurichloride, nitrate, sulphate, hydrogen sulphate, picrate, and picrolonate are described.

The nitrosoamine, $C_{11}H_{13}N_3 \cdot NO$, darkens at 99° and melts at $106-107^\circ$. When the alkaloid is left with acetyl chloride for a few weeks, a steel-blue hydrochloride is produced, whilst if the mixture is heated for six hours in a sealed tube, a dark brown hydrochloride is formed. When treated with methyl iodide, the base is converted into its hydriodide, together with two other compounds which have not yet been investigated. If the alkaloid is digested with concentrated sulphuric acid, a product is obtained which is probably a sulphonic acid. E. G.

A New Highly Fluorescent Substance Derived from Physostigmine [Eserine]. PAUL GAUBERT (*Compt. rend.*, 1909, 149, 852—853).—When an aqueous solution of eserine is kept for several months, it acquires a deep blue tint, and on the addition of phthalic acid develops a red fluorescence which exceeds in intensity that of all known substances. The compound to which this is due has been isolated as dark blue crystals. W. O. W.

Constitution of Stachydrine. ERNST SCHULZE and G. TRIER (*Ber.*, 1909, 42, 4654—4659. Compare Abstr., 1909, i, 323).—The constitution of stachydrine as the methylbetaine of hygric acid (dimethylbetaine of α -proline) is proved by its conversion into derivatives of hygric acid (Willstätter and Ettlinger, Abstr., 1903, i, 272), and its synthesis from this acid.

The ethyl ester of stachydrine hydrochloride forms a syrup, and yields a sparingly soluble aurichloride, $C_9H_{13}O_2NaAuCl_4$, m. p. $59-60^\circ$. When distilled, the hydrochloride of the ester gives a 20% yield of ethyl hygrate, b. p. $77-79^\circ/18$ mm.

Stachydrine has been synthesised by converting ethyl hygrate

(ethyl 1-methylpyrrolidine-2-carboxylate) into its methiodide (Willstätter and Ettlinger, *loc. cit.*, 364), and then treating this with silver oxide.

Stachydrine platinichloride, $2C_7H_{12}O_2N, H_2PtCl_6$, crystallises in long, yellow needles. J. J. S.

Synthesis of Indolenine Ketones. GIUSEPPE PLANCHER and D. GIUMELLI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 393—397).—

3:3-Dimethylindolenine-2-carboxylonitrile, $C_6H_4 \begin{smallmatrix} \text{N} \\ \text{CMe}_2 \end{smallmatrix} \text{C} \cdot \text{CN}$, previously described as a liquid (Abstr., 1899, i, 543), has been obtained in the solid state, m. p. about 38° .

3:3-Dimethylindolenyl 2-methyl-ketone, $C_6H_4 \begin{smallmatrix} \text{N} \\ \text{CMe}_2 \end{smallmatrix} \text{C} \cdot \text{COMe}$, prepared by the action of magnesium methyl iodide on the preceding compound, forms volatile needles, m. p. 130° , is readily resinified by acids, and gives the iodoform reaction with iodine and alkali. With hydroxylamine it gives the oxime, m. p. $175\text{--}176^\circ$, formed by the action of nitrous acid on 3:3-dimethyl-2-ethylindolenine (compare Abstr., 1903, i, 433). The corresponding semicarbazone, $C_{13}H_{16}ON_4$, forms scales, m. p. 242° .

The action of magnesium phenyl bromide on 3:3-dimethylindolenine-2-carboxylonitrile yields, not a ketone, but the imino-compound, $C_6H_4 \begin{smallmatrix} \text{N} \\ \text{CMe}_2 \end{smallmatrix} \text{C} \cdot \text{CPh} \cdot \text{NH}$, m. p. $103\text{--}5^\circ$. This imino-derivative is the first intermediate compound formed in Blaise's reaction (Abstr., 1901, i, 133), which proceeds according to the equations: (1) $R \cdot \text{CN} + \text{MgR}' \cdot \text{Br} = \text{CRR}'_2 \cdot \text{NMgBr}$; (2) $\text{CRR}'_2 \cdot \text{NMgBr} + \text{H}_2\text{O} = \text{CRR}'_2 \cdot \text{NH} + \text{MgBr} \cdot \text{OH}$, and (3) $\text{CRR}'_2 \cdot \text{NH} + \text{H}_2\text{O} = \text{R} \cdot \text{CO} \cdot \text{R}'_2 + \text{NH}_3$. The above imino-compound does not readily give phase (3) of the reaction, but the imino-group present reacts easily with ketone reagents; thus, the compound gives an oxime, $C_{11}H_{16}ON_2$, which forms prisms, m. p. 205° , and a p-nitrophenylhydrazone, m. p. 209° .

T. H. P.

Catalytic Hydrogenation of Aromatic and Quinoline Bases. GEORGES DARZENS (*Compt. rend.*, 1909, 149, 1001—1004. Compare Padoa, Abstr., 1906, i, 765; Ipatieff, Abstr., 1908, i, 332).—1:2:3:4-Tetrahydroquinoline is formed when quinoline is hydrogenated at $160\text{--}180^\circ$ in presence of nickel which has been obtained by reduction of its hydroxide at $250\text{--}255^\circ$. The product is free from indole and from more highly hydrogenated quinolines. 6-Methyl-tetrahydroquinoline has been obtained in the same way.

The reduction products of dimethyl- and diethyl-aniline have been investigated by Senderens (Abstr., 1904, i, 660), but have been obtained by the present author in a state of greater purity. cyclo-Hexyldimethylamino has b. p. 159° , and forms a *picrate*, m. p. $176\text{--}177^\circ$; the corresponding diethyl derivative has b. p. 191° , and forms a *picrate*, m. p. $91\text{--}92^\circ$.

Attention is drawn to the influence of the temperature at which the nickel is prepared on its behaviour as a catalyst. W. O. W.

Bz-Sulphoquinolinecarboxylic Acids. ALBERT EDINGER and L. BÜHLER (*Ber.*, 1909, 42, 4313—4320).—In connexion with their work on *Bz*-quinoline mercaptans (*Abstr.*, 1908, i, 363) the authors have prepared the following substances.

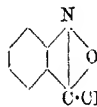
5-Sulphoquinoline-8-carboxylic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{NH}_5\cdot\text{SO}_3\text{H}$, is obtained by oxidising 8-methylquinoline-5-sulphonic acid (Herzfeld, *Abstr.*, 1884, 1198) by chromic and sulphuric acids, and is separated from the unchanged material by crystallisation from dilute sulphuric acid, D 1.16, at 75° ; the copper and the barium salts are mentioned.

6-Methylquinoline-7-sulphonic acid has been prepared by the Skraup reaction, but is obtained in good yield by working under the author's conditions. When heated at 260 — 270° with a mixture of equal parts of potassium and sodium hydroxides and a little water, it yields 7-hydroxy-6-methylquinoline, m. p. 244° , b. p. $240^\circ/22$ mm., whilst by distilling its sodium salt with potassium cyanide, 7-cyano-6-methylquinoline, m. p. 133° , is obtained. 7-Sulphoquinoline-6-carboxylic acid is obtained from 6-methylquinoline-7-sulphonic acid by oxidation with chromic and sulphuric acids; it crystallises in white octahedra, and the strontium and barium salts are mentioned. By fusion with equal parts of potassium and sodium hydroxides at 275° , a dihydroxyquinoline, darkening at 280° and m. p. 321° , is obtained, which crystallises in large, yellow needles, and contains its hydroxyl groups in positions 6 and 7, assuming that intramolecular change has not occurred during the fusion with the alkalis.

8-Sulphoquinoline-6-carboxylic acid and 6-sulphoquinoline-8-carboxylic acid are obtained from the corresponding toluquinolinesulphonic acids by processes of oxidation similar to the preceding.

The reaction between sodium 6-sulphoquinoline-8-carboxylate and phosphorus pentachloride at 125 — 135° yields the sulphonyl chloride, which is reduced by stannous chloride and hydrochloric acid; the resulting tin double salt is decomposed by sodium hydroxide, yielding the corresponding mercaptide, which is converted by the Schotten-Baumann process into the benzoyl derivative, m. p. 213° , of quinoline-6-mercaptan-8-carboxylic acid. C. S.

Reduction of *o*-Nitrophenylpropionic Acid. GUSTAV HELLER and WALTER TISCHNER (*Ber.*, 1909, 43, 4555—4566).—On reduction of *o*-nitrophenylpropionic acid, indigotin and *o*-aminophenylpropionic acid have been obtained. When reduction is carried out with zinc



dust in ammoniacal solution, a ring compound, homoanthroxanic acid (annexed formula), is formed. This crystallises in lustrous, flat needles with a faint yellow shimmer; m. p. 108° . It is a strong carboxylic acid; the alcoholic aqueous solution reddens litmus; it dissolves in presence of sodium and barium carbonates and sodium acetate. The silver salt contains one atom of metal. It is not easily esterified or acetylated, reduces ammoniacal silver and Fehling's solutions on boiling, and gives no coloration with ferric chloride.

When heated at 110–120° it is converted into methylanthrothane,
 $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{Me} \end{smallmatrix} \text{O}$. Sodium nitrite converts it into the *oxime* of

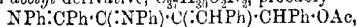
anthroxanaldehyde, $\begin{smallmatrix} \text{N} \text{---} \text{O} \\ | \quad | \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{CH} \cdot \text{N} \cdot \text{OH} \end{smallmatrix}$, crystallising in colourless needles, m. p. 172–173°, which can also be prepared from anthroxanaldehyde and hydroxylamine.

On reduction, homoanthroxanic acid at first forms *o*-aminobenzoyl-acetic acid, which immediately condenses to the anhydride, 4-ketohydrocarbostyryl, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \text{---} \text{C} \cdot \text{OH} \\ \diagdown \quad \diagup \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix}$, which crystallises in bunches of colourless, hexagonal plates, and is identical with the 4-hydroxycarbostyryl described by Baeyer and Bloem (Abstr., 1883, 196); the benzoyl derivative forms radially-grouped, colourless needles, m. p. 220°.

Homoanthroxanic acid, when warmed with hydrochloric acid, is converted into 2 : 3-dihydroxy-4-quinolone, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NH} \cdot \text{C} \cdot \text{OH} \\ | \quad | \\ \text{CO} \cdot \text{C} \cdot \text{OH} \end{smallmatrix}$ or $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \text{---} \text{C} \cdot \text{OH} \\ \diagdown \quad \diagup \\ \text{CO} \cdot \text{CH} \cdot \text{OH} \end{smallmatrix}$, which forms long, colourless needles, m. p. 276° (decomp.), and gives a characteristic, stable, violet coloration with ferric chloride. The benzoyl derivative crystallises in colourless, matted needles, m. p. 216–217° (decomp.). On treatment with phosphorus pentachloride, two crystalline products are obtained: needles, m. p. 85°, volatile in steam, and non-volatile needles, m. p. 205–220°. It is converted into 4-ketohydrocarbostyryl on reduction.

E. F. A.

Condensation of α -Diketones with Aldehydes and Primary Arylamines. WALTHER BORSCHKE and J. CAMPER TITSINGH (*Ber.*, 1909, 42, 4283–4287. Compare Abstr., 1909, i, 955).—When α -diketones are allowed to react with aldehydes and arylamines under conditions similar to those used in the preparation of cinchonic acids from pyruvic acid, aldol condensation occurs (in one case 2 molecules of the aldehyde reacting with one of the ketone), and the resulting product forms an anil with the arylamine. Thus aniline, benzaldehyde, and acetylbenzoyl (Abstr., 1907, i, 326) react in hot alcoholic solution, yielding *acetylbenzoyl- α -diphenyl- β -phenylglyoxylpropanedianil*, $\text{NPh} \cdot \text{CPh} \cdot \text{C}(\text{NPh}) \cdot \text{CH}(\text{CHPh} \cdot \text{OH})_2$, which crystallises from glacial acetic acid in yellow needles, m. p. 176° (decomp.). When heated with acetic anhydride and anhydrous sodium acetate, the anil yields an *acetyl* derivative, $\text{C}_{37}\text{H}_{30}\text{O}_3\text{N}_3$, probably



which crystallises in colourless needles, m. p. 273°.

When salicylaldehyde is substituted for benzaldehyde in the above condensation, a resin is formed, but with anisaldehyde, *δ -phenyl- α -anisyl- Δ^2 -butene- δ -dianil*, $\text{NPh} \cdot \text{CPh} \cdot \text{C}(\text{NPh}) \cdot \text{CH} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OCH}_3$, is formed, crystallising in needles, m. p. 153°.

VOL. XXVIII. i.

m-Nitrobenzaldehyde yields a similar *anil*,
 $\text{NPh}:\text{CPh}\cdot\text{C}(\text{NPh})\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$,
 in the form of yellow needles, m. p. 181° .
o-Phenyl- δ -anisyl- Δ^2 -butene- $\gamma\delta$ -dianil,
 $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NPh})\cdot\text{C}(\text{NPh})\cdot\text{CH}:\text{CHPh}$,
 obtained from aniline, benzaldehyde, and acetyl-*p*-anisoyl, forms
 colourless needles, m. p. 203° . When *p*-anisidine is substituted for
 aniline, the *p*-*anisil*,
 $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})\cdot\text{C}(\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})\cdot\text{CH}:\text{CHPh}$,
 is obtained as yellow needles, m. p. 158° .
Dicinnamoyldianil, $\text{CHPh}:\text{CH}\cdot\text{C}(\text{NPh})\cdot\text{C}(\text{NPh})\cdot\text{CH}:\text{CHPh}$, ob-
 tained from diacetyl, benzaldehyde, and aniline in glacial acetic acid
 solution, forms a yellow, crystalline powder, m. p. 270° .
 Acetylbenzoyl, benzaldehyde, and *m*-nitroaniline do not condense.
 J. J. S.

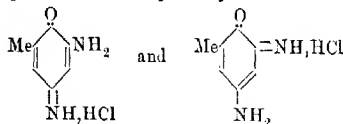
Auxochromic Action of Amino- and Aminophenyl Groups.
 JEAN PICCARD (*Ber.*, 1909, 42, 4332—4341).—The intense colour of
 Wurster's salts and of many dyes, particularly of the triphenyl-
 methane series, is attributed by Willstätter and Piccard (*Abstr.*, 1908,
 i, 475) to the *meri*-quinonoid constitution of such substances. This
 view is contraverted by Kehrman (*Abstr.*, 1908, i, 699), who main-
 tains, in consequence of the behaviour of the aminobenzoquinone-
 imines (*Abstr.*, 1906, i, 967), that the intense colour is due to the
 influence of a quinonoid benzene nucleus increased by an auxochromic
 amino-group. The author shows that by oxidising 3:5-diamino-*o*-
 cresol dihydrochloride in a freezing mixture by an excess of ferric
 chloride, and adding a saturated solution of potassium nitrate, a light
 red *holo*-quinonoid *amino-o-toluquinoneimine nitrate*, $\text{C}_7\text{H}_5\text{O}_2\text{N}_3$, is
 obtained, which does not show any resemblance to true red dyes in its
 behaviour in light. When the oxidation is performed with a deficiency
 of ferric chloride, a dark red *meri*-quinonoid compound is obtained.
 Also, in solution, Kehrman's red compounds (*loc. cit.*) differ essentially
 from red dyes; the latter exhibit pronounced selective absorption,
 whilst the former show no trace of a band.

Coloured quinonoid substances are classified in two groups: (1)
 Colour is due to a quinonoid nucleus and an auxochromic amino-
 group; (2) colour is due to the junction of quinonoid and hydro-
 quinonoid nuclei (*meri*-quinonoid compounds). The preceding light red
 nitrate is typical of group (1), Wurster's red salt of group (2).

The difference in the colour of triphenylmethanimine bases and
 their salts is attributed by Kehrman to a change in the constitution
 of the chromophore. From the spectroscopic examination of magenta,
 the author considers that the triphenylmethane dyes are *meri*-
 quinonoid compounds belonging to group (2). Substances which con-
 tain only an auxochromic amino-group in addition to the quinonoid
 nucleus are not dyes.

When an aqueous solution of diaminocresol dihydrochloride is
 oxidised by an excess of ferric chloride in the presence of saturated
 sodium chloride, a light red aminotoluquinoneimine hydrochloride
 crystallises at -15° , and a dark red isomeride at the ordinary

temperature. The former is regarded as the *p*-quinonoid and the latter as the *o*-quinonoid form respectively:



C. S.

A Reaction of Polybasic Acids and a New Reaction for Titanium. JEAN PICCARD (*Ber.*, 1909, 42, 4341—4345).—It is well known that the reduction of organic substances by titanous chloride is accelerated by the addition of potassium sodium tartrate. The author finds that indigotin, Wurster's red, and, in particular, aminotoluquinoneimine hydrochloride (preceding abstract) are very slowly affected by titanous chloride in aqueous or dilute hydrochloric acid solution, but the addition of certain acids, such as tartaric acid, increases the rate of reduction enormously. An examination of about fifty inorganic and organic acids reveals the fact that, in general, polybasic acids exert an accelerative influence, but not so monobasic acids. The most marked effect is produced by hydrofluoric acid (an argument in favour of the polymerised state, H_2F_2), oxalic, glycollic, lactic, pyruvic, tartaric, malic, and citric acids, catechol, and pyrogallol. The remaining halogen acids, and formic, acetic, propionic, butyric, benzoic, β -naphthoic, and monochloroacetic acids have no influence.

Catechol produces with a solution of titanous chloride a yellowish-orange coloration, which is much more intense than that produced by oxalic acid. The test, which is fifteen times more sensitive than the hydrogen peroxide test, should be performed with an excess of catechol and in the absence of mineral acids, and preferably also of alkali hydroxides and carbonates and ammonium hydroxide.

The author suggests that Fenton's brown substance, obtained from dihydroxymaleic acid and compounds of quadrivalent titanium (*Trans.*, 1908, 93, 1064), may contain trivalent titanium. C. S.

Diketodialkylpiperazines. KARL W. ROSENMUND (*Ber.*, 1909, 42, 4470—4481).—The author has prepared a number of diketodialkylpiperazines in order to investigate the hypnotic action of the alkyl groups, more especially of the ethyl group, in them. 2:5-Diketod:6-diethylpiperazine exhibits no such action, although, like veronal, it contains two ethyl groups combined with a quaternary carbon atom occurring in a physiologically indifferent ring-system.

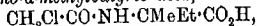
α -Bromo- α -ethylbutyric acid (compare Kalle & Co., *Abstr.*, 1907, i, 276) forms white scales, m. p. 20°, b. p. 130—133°/18 mm., and may be prepared in almost theoretical yield by the action of bromine on α -ethylbutyric acid in a sealed tube at 136—140°. Its ethyl ester is a colourless liquid, b. p. 87—88°/18 mm. (impure), with an intense camphor-like odour.

α -Amino- α -ethylbutyric acid (compare Gulewitsch and Wasmus, *Abstr.*, 1906, i, 409) is best prepared by the action of methyl-alcoholic VOL. XXVIII. i.

J

ammonia on α -bromo- α -ethylbutyric acid, its preparation from diethyl ketone by Zelinsky and Stadnikoff's method (Abstr., 1906, i, 425) being difficult and infertile. Its ethyl ester, $\text{NH}_2 \cdot \text{C}(\text{Et})_2 \cdot \text{CO}_2\text{Et}$, is a colourless oil, b. p. 76—77°/15 mm.

α -Chloroacetyl-amino- α -methylbutyric acid,



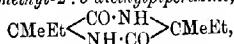
prepared by the action of chloroacetyl chloride and sodium hydroxide on α -amino- α -methylbutyric acid, forms colourless needles, m. p. 162°.

α -Glycylamino- α -methylbutyric acid, $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}(\text{Me})\text{Et} \cdot \text{CO}_2\text{H}$, prepared by the action of aqueous ammonia on α -chloroacetyl-amino- α -methylbutyric acid, forms white needles, m. p. 245° (decomp.).

3:6-Diketo-2-methyl-2-ethylpiperazine, $\text{C}(\text{Me})\text{Et} \cdot \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \cdot \text{CH}_2$, prepared by the action of ammonia either on a methyl-alcoholic solution

of ethyl α -glycylamino- α -methylbutyrate at 0°, or on ethyl α -chloroacetyl-amino- α -methylbutyrate at 100°, forms slender, white needles, m. p. 250°.

3:6-Diketo-2:5-dimethyl-2:5-diethylpiperazine,



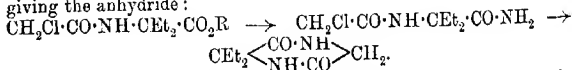
prepared by heating ethyl α -amino- α -methylbutyrate in a sealed tube at 240—250°, forms slender needles, subliming on heating, and having m. p. 336° in a closed capillary tube.

α -Chloroacetyl-amino- α -ethylbutyric acid, $\text{CH}_2\text{Cl} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}(\text{Et})_2 \cdot \text{CO}_2\text{H}$, forms small needles or prisms, m. p. 190°.

α -Glycylamino- α -ethylbutyric acid, $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}(\text{Et})_2 \cdot \text{CO}_2\text{H}$, forms white crystals, m. p. 269° (decomp.).

3:6-Diketo-2:2-diethylpiperazine, $\text{C}(\text{Et})_2 \cdot \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \cdot \text{CH}_2$, prepared by the action of methyl-alcoholic ammonia at 105° on ethyl α -chloroacetyl-amino- α -ethylbutyrate, forms long, shining needles, m. p. 272°, having an extremely bitter taste.

Ethyl α -glycylamino- α -ethylbutyrate, m. p. 202—210°, when heated with alcoholic ammonia at 100°, yields only the corresponding free acid, m. p. 269°. This result is not in accord with Fischer's views on the mechanism of the formation of the anhydrides of amino-acids from the esters of halogen-acylamino-acids by the action of ammonia, since, according to these views, the dipeptide esters are formed as intermediate products and give the anhydrides by loss of alcohol. It seems, on the contrary, that the alkoxy-group is first replaced by an amino-group, the amide thus formed losing hydrogen chloride and giving the anhydride:



That such an intermediate amide can be formed is shown by the action of ammonia on the ethyl ester of bromodiethylacetyl-glycine (*vide infra*).

Ethyl bromoethylbutyrylaminoacetate, $\text{C}(\text{Et})_2\text{Br} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, prepared by the action of bromoethylbutyryl chloride on ethylaminoacetate, has m. p. 35—36°.

Bromoethylbutyrylglycinamide, $\text{CET}_2\text{Br}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, obtained by the action of methyl-alcoholic ammonia on the preceding ester, has m. p. 109—110°. This compound exhibits little inclination to ring-closure, and on heating for several hours with methyl-alcoholic ammonia at 100—105°, it yields (1) two isomeric compounds, m. p. 122° and 87—88°, which are apparently the two stereoisomeric α -ethylrotonylglycinamides, $\text{CHMe}\cdot\text{CEt}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ (compare Mannich and Zernik, Abstr., 1908, i, 399), and (2) small quantities of two compounds, m. p. 99—100° and 110° respectively. With pyridine in place of ammonia, a similar reaction occurs.

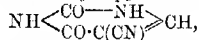
T. H. P.

Pyrimidines. XLVIII. Synthesis of 5-Cyanouracil. TREAT B. JOHNSON (*Amer. Chem. J.*, 1909, 42, 505—515).—The work described in this paper was undertaken for the purpose of preparing certain pyrimidines to be used for the synthesis of new thymine derivatives. It has been shown by Wheeler, Johnson, and Johns (Abstr., 1907, i, 559) that ethyl ethoxymethylenemalonate condenses with ψ -thiocarbamides with formation of esters of 2-alkylthiol-6-pyrimidone-5-carboxylic acids, which are readily hydrolysed by hydrochloric acid with production of uracil-5-carboxylic acid. It therefore seemed probable that 5-cyanouracil could be obtained in an analogous manner from ethyl cyanoethoxymethyleneacetate. Experiments have been carried out which show that ethyl- ψ -thiocarbamide condenses with this ester in presence of alkali hydroxide with formation of 5-cyano-2-ethylthiol-6-pyrimidone, together with smaller quantities of ethyl 6-amino-2-ethylthiopyrimidine-5-carboxylate (Wheeler and Johns, Abstr., 1907, i, 1083). On hydrolysing the former product with sulphuric acid, a quantitative yield of 5-cyanouracil is obtained.

On adding ethyl cyanoethoxymethyleneacetate (1 mol.) to an alcoholic solution of ethyl- ψ -thiocarbamide (1 mol.), *ethyl α -cyano- β -ethyl- ψ -thiocarbamidoacrylate*, $\text{NH}_2\cdot\text{C}(\text{SEt})\cdot\text{N}\cdot\text{CH}\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$, m. p. 130° (decomp.), separates in yellow crystals, and, when warmed with alkali hydroxide, is converted into *5-cyano-2-ethylthiol-6-pyrimidone*, $\text{NH}\langle\begin{smallmatrix} \text{C}(\text{SEt})=\text{N} \\ \text{CO}\cdot\text{C}(\text{CN}) \end{smallmatrix}\rangle\text{CH}$, m. p. 222°, which crystallises in prisms. If ethyl cyanoethoxymethyleneacetate (1 mol.) is added to an alcoholic solution of ethyl- ψ -thiocarbamide (1.7 mols.), *α -cyano- β -ethyl- ψ -carbamidoacrylethyl- ψ -thiocarbamide*,

$\text{NH}_2\cdot\text{C}(\text{SEt})\cdot\text{N}\cdot\text{CH}\cdot\text{C}(\text{CN})\cdot\text{CO}\cdot\text{N}\cdot\text{C}(\text{SEt})\cdot\text{NH}_2$, m. p. 164—165° (decomp.), is produced, which crystallises in prisms; this compound is converted by warm sodium hydroxide into 5-cyano-2-ethylthiol-6-pyrimidone and by concentrated hydrochloric acid into 5-cyanouracil.

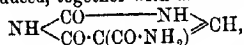
5-Cyanouracil (2 : 6-diketo-5-cyanopyrimidine),



m. p. 295° (decomp.), crystallises in prisms, and by the action of concentrated hydrochloric acid is converted quantitatively into uracil.

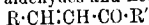
When 5-cyano-2-ethylthiol-6-pyrimidone is dissolved in concentrated

hydrochloric acid and the solution evaporated to dryness at 100°, 5-cyanouracil is produced, together with *uracil-5-carboxylamid*,



which forms small prisms, does not melt below 300°, and is converted quantitatively into uracil by concentrated hydrochloric acid. E. G.

Influence of Constitution on the Conversion of Phenylhydrazones of Unsaturated Compounds into Pyrazolines. KARL AUWERS and H. VOSS (*Ber.*, 1909, 42, 4411—4427).—The method recently described for converting into pyrazolines the phenylhydrazones of unsaturated aldehydes and ketones of the type



(*Abstr.*, 1909, i, 59) is now employed to determine how far the readiness to undergo this change is affected by the constitution of the groups R and R'. This paper deals with the aromatic unsaturated aldehydes and ketones. The phenylhydrazone of phenyl styryl ketone changes into 1:3:5-triphenylpyrazoline even at low temperatures, and cannot be isolated; the phenylhydrazones of cinnamaldehyde and styryl methyl ketone, however, only form pyrazolines at a high temperature. The phenylhydrazones of the following ketones are stable: styryl ethyl ketone, styryl *n*-propyl ketone, styryl *n*-butyl ketone, styryl *n*-nonyl ketone; those of styryl isopropyl ketone and styryl *tert*-butyl ketone are unstable, especially the latter. Hence the structure of the group R', rather than its weight, seems of importance.

The introduction of an hydroxyl or methoxy-group into the ortho-position in one of the benzene nuclei favours the formation of pyrazolines. From *o*-hydroxystyryl ethyl and propyl ketones only the pyrazolines can be obtained. *o*-Methoxystyryl ethyl ketone and phenylhydrazine also yield a pyrazoline directly. The introduction of a nitro-group has the opposite effect: phenyl *m*- and *p*-nitrostyryl ketones yield phenylhydrazones which are converted into pyrazolines only on boiling with glacial acetic acid. The *p*-nitrophenylhydrazone of cinnamaldehyde cannot be converted into a pyrazoline even by means of this reagent. Furfurylideneacetone behaves like styryl methyl ketone. Cinnamylideneacetophenone yields a stable phenylhydrazone.

For distinguishing between phenylhydrazones and pyrazolines, Knorr's reaction is not to be depended on in every case; reduction with sodium amalgam is a safer criterion; under this treatment all phenylhydrazones yield aniline. *Cinnamaldehyde-p-bromophenylhydrazone* forms yellow needles, m. p. 139—140°; when boiled with glacial acetic acid it yields 5-phenyl-1-*p*-bromophenylpyrazoline, which crystallises in yellow needles, m. p. 140°. 1:5-Diphenyl-3-methylpyrazoline (from styryl methyl ketone) has m. p. 115—116° (Knorr gave 109°: *Abstr.*, 1885, 555). Styryl ethyl ketone-phenylhydrazone has m. p. 104—105° (Harries and Müller gave 101°: *Abstr.*, 1902, i, 295).

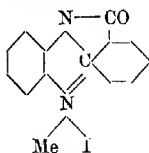
1:5-Diphenyl-3:4-dimethylpyrazoline, prepared from a methyl styryl

ethyl ketone-phenylhydrazone, has m. p. 82—83°. *Styryl isopropyl ketone* has b. p. 147°/11 mm.; the 1:5-diphenyl-3-isopropylpyrazoline obtained from it forms white needles, m. p. 88·5°. *Styryl n-butyl ketone* has b. p. 159—167°/11 mm., and m. p. 38—39°; the phenylhydrazone has m. p. 97·5—98·5°. 1:5-Diphenyl-3-tert-butylpyrazoline (from styryl tert-butyl ketone) has m. p. 108—108·5°. *Styryl n-nonyl ketone-phenylhydrazone* crystallises in silky, felted needles, m. p. 76—77°; when heated with glacial acetic acid it gives a pyrazoline in brown crystals, m. p. 60°. *o*-Hydroxystyryl ethyl ketone has m. p. 118—119° (Decker and von Fellenberg, Abstr., 1909, i, 116, give 101°); with phenylhydrazine, it yields directly 1-phenyl-5-*o*-hydroxyphenyl-3-ethylpyrazoline, which crystallises in small needles, m. p. 134°. The substance of m. p. 119°, which Harries and Busse (Abstr., 1896, i, 301) obtained from *o*-hydroxystyryl *n*-propyl ketone, is not, as they assumed, the phenylhydrazone, but 1-phenyl-5-*o*-hydroxyphenyl-3-propylpyrazoline. When heated with glacial acetic acid it yields a compound, m. p. 98—99°, which does not give the pyrazoline reaction. The supposed phenylhydrazone, obtained by the same authors (*loc. cit.*) from phenyl-*o*-hydroxystyryl ketone, is 1:3-diphenyl-5-*o*-hydroxyphenylpyrazoline; it yields a mono benzoyl derivative, m. p. 172°. *o*-Methoxystyryl ethyl ketone, a yellow oil, gives 1-phenyl-5-*o*-methoxyphenyl-3-methylpyrazoline, which forms yellow needles, m. p. 87—88°. *p*-Nitrostyryl methyl ketone-phenylhydrazone forms red crystals, m. p. 195—196°; when heated with glacial acetic acid, it yields 1-phenyl-5-*p*-nitrophenyl-3-methylpyrazoline, which crystallises in small, golden-yellow needles, m. p. 112—113°. Phenyl *m*-nitrostyryl ketone-phenylhydrazone has m. p. 101—103°; boiling glacial acetic acid converts it into 1:3-diphenyl-5-*m*-nitrophenylpyrazoline, which forms brownish-yellow needles, m. p. 122—123°. Phenyl *p*-nitrostyryl ketone-phenylhydrazone crystallises in felted, red needles, m. p. 138—139°; it yields 1:3-diphenyl-5-*p*-nitrophenylpyrazoline, which forms brownish-yellow needles, m. p. 113—114°. Furfurylideneacetone has b. p. 112—115°/10 mm.; its phenylhydrazone forms yellow needles, m. p. 131—132°; 1-phenyl-5-furyl-3-methylpyrazoline crystallises in large, white needles, which are volatile in steam, and have m. p. 102—103°. Cinnamylideneacetophenonephenylhydrazone has m. p. 156—158° (Sorge, Abstr., 1902, i, 379, gave 125—126°). R. V. S.

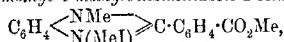
Benzoylenebenzimidazole. HANS RUPE and K. G. THIES [and, in part, with ALEX. WETTER] (*Ber.*, 1909, 42, 4287—4304).—*o*-Benzoylenebenzimidazole (Thiele and Falk, Abstr., 1906, i, 751) can be prepared by reducing *o*-nitrophthalanil with stannous chloride and hydrochloric acid, or, better (75% of theory), with iron and acetic acid. It crystallises in long, yellow needles with a silky lustre, m. p. 212—213°, and is readily hydrolysed by acids or alkalis to phenylbenzimidazole-*o*-carboxylic [benzimidazole-2-benzoic] acid, m. p. 266° (Thiele and Falk, 273°). The hydrochloride of the acid forms long, lustrous needles. The methyl ester, $C_{15}H_{12}O_2N_2$, crystallises in glistening, colourless needles, m. p. 188°. The aurichloride of the ethyl ester, $[C_{16}H_{14}O_2N_2, AuCl_3]$, forms slender, orange-yellow needles, m. p. 120°. When the ethyl ester is

heated, it yields alcohol and the iminazole. The *phenylhydrazide* of the acid, $C_6H_4 \cdot \begin{smallmatrix} \text{NH} \\ \text{N} \end{smallmatrix} \gg C \cdot C_6H_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{NHPh}$, crystallises in colourless needles, m. p. 244°.

Benzoylenebenziminazole methiodide (annexed formula), obtained by heating the iminazole with excess of methyl iodide in sealed tubes at 90–100°, crystallises in slender, bright red needles, m. p. about 200°. When carefully heated above its m. p., it yields methyl iodide and the benziminazole, and when boiled with water yields *benziminazole-2-benzoic acid methiodide*, $C_6H_4 \cdot \begin{smallmatrix} \text{NH} \\ \text{N}(\text{MeI}) \end{smallmatrix} \gg C \cdot C_6H_4 \cdot \text{CO}_2\text{H}$, which crystallises in glistening, yellow cubes, m. p. 200–210°.



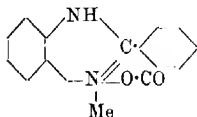
The *methiodide* of the methyl ester, $C_{16}H_{15}O_2N_2I$, is obtained by the action of methyl alcohol on the red methiodide at 90–100°. The *methiodide* of *methyl 1-methylbenziminazole-2-benzoate*,



obtained (a) by heating benzoylenebenziminazole with excess of methyl iodide and a little methyl alcohol at 120°, (b) by heating the methyl ester of the acid with methyl iodide (2 mols.) and a little methyl alcohol at 100°, or (c) by heating the methiodide of the methyl ester with methyl iodide at 100°, crystallises in large, compact prisms, m. p. 230°.

The *methiodide* of the ethyl ester, $C_{17}H_{17}O_2N_2I$, forms compact prisms, m. p. 191°. The *methiodide* of *ethyl 1-methylbenziminazole-2-benzoate*, $C_{18}H_{19}O_2N_2I$, crystallises in colourless needles or long prisms, m. p. 175°.

When heated with ammonium hydroxide solution or with sodium acetate solution at the ordinary temperature, the methiodide of the 2-benzoic acid yields the *betaine* (annexed formula), which crystallises in minute needles, m. p. 280–281°. Its constitution as a betaine is based on the following properties: it dissolves readily in alkali carbonate solutions, and the addition of hydrochloric acid precipitates the methochloride of benziminazole-2-benzoic acid. When heated with acetic anhydride and hydriodic acid, it yields the red methiodide of benzoylenebenziminazole. When heated for some time at 280–290°, it yields benzoylenebenziminazole, methyl alcohol, and unaltered substance.



The *methochloride* of benziminazole-2-benzoic acid, $C_{15}H_{13}O_2N_2Cl$, crystallises in colourless needles, m. p. 272–274°, and with acetic anhydride yields *benzoylenebenziminazole methochloride*, $C_{15}H_{11}ON_2Cl$, greenish-yellow needles, m. p. 200°. The *methobromide* of the acid, $C_{15}H_{13}O_2N_2Br$, has m. p. about 270°, and the *methobromide* of the benzoylenebenziminazole forms yellow needles, m. p. about 230°. When the methiodide of methyl 1-methylbenziminazole-2-benzoate is shaken with moist silver oxide, the corresponding *ammonium* base, $C_{17}H_{15}O_2N_2$, is obtained as a white solid, m. p. 252°.

When benzoylenobenziminazole is covered with nitric acid (D 1.52) and acetic anhydride is added, drop by drop, at 0° , a *nitro-derivative*, I, $C_{14}H_9O_3N_3$, which crystallises in pale yellowish-green needles, m. p. 239° , is formed, together with *nitrobenziminazole-2-benzoic acid*, $C_{14}H_9O_4N_3$, colourless needles, m. p. $280-300^{\circ}$ (decomp.).

An isomeride, *nitrobenzoylenebenziminazole*, II, is formed when nitric acid (D 1.25) is added to a solution of the iminazole in acetic anhydride; it crystallises in small, brown needles, m. p. 280° (decomp.), and is accompanied by a nitrobenziminazole-2-benzoic acid, which crystallises in orange-coloured needles, m. p. $280-300^{\circ}$ (decomp.). This second nitro-acid is a powerful dye.

Aminobenzoylenebenziminazole, I, $C_{14}H_9ON_3$, obtained by reducing the nitro-compound, I, with sodium hyposulphite, crystallises in brilliant red, flat needles, m. p. $298-305^{\circ}$. Its *acetyl derivative*, $C_{16}H_{11}O_2N_3$, forms yellow needles, decomposing at 253° . The base is a dye, and when diazotised and coupled with phenols yields valuable *azo-dyes*.

o-Nitrophthalanil, $NO_2 \cdot C_6H_4 \cdot N \cdot C_2O_2 \cdot C_6H_4$, obtained by condensing *o*-nitroaniline and phthalic anhydride with sodium acetate, crystallises in pale yellow needles, m. p. 203° . It is stable towards acids, but is readily decomposed by alkalis, and when reduced with a concentrated sodium hyposulphite solution yields *o-aminophthalanil*, $NH_2 \cdot C_6H_4 \cdot N \cdot C_2O_2 \cdot C_6H_4$, which crystallises in brilliant yellow needles, m. p. $188-189^{\circ}$. The *acetyl derivative*, $C_{16}H_{12}O_3N_2$, forms colourless needles, m. p. 202° ; the *hydrochloride*, glistening, colourless needles. When diazotised and coupled with resorcinol, the base yields an *azo-dye*, $C_{20}H_{13}O_4N_3$, as golden-brown plates, m. p. 190° . J. J. S.

Indigotin. II. Indigotin Diarylimides. EUGÈNE GRANDMOUGIN and ED. DESSOULAVY (*Ber.*, 1909, 42, 4401-4407. Compare Abstr., 1909, i, 968).—*Indigotindianilide hydrochloride*, prepared by the interaction of indigotindianilide in acetic acid with alcoholic hydrogen chloride, forms dark bluish-green needles. The corresponding *sulphate* is very similar.

Dehydroindigotindianilide nitrate is prepared by adding four times its weight of 50% nitric acid to indigotindianilide, which immediately changes its blue colour to a brilliant red. The nitrate crystallises in rosettes of red needles; the alcoholic solution is turned violet by alcoholic potassium hydroxide, but on heating it turns a dirty green, and indigotindianilide separates. To obtain the corresponding base, the nitrate is suspended in pyridine and oxidised with lead peroxide, whereby a brownish-red, crystalline substance is obtained, which yields red salts with acids and is partly converted on heating into indigotindianilide. The nitrate is a tetranitrate, but part of the nitric acid is lost during drying.

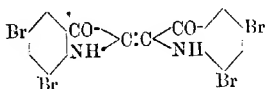
Dehydroindigotindi-p-toluidide tetranitrate resembles the anilide, and gives the characteristic violet coloration with potassium hydroxide. The corresponding *tetrahydrochloride* forms a red, crystalline precipitate.

7:7'-Dimethylindigotindi-p-toluidide, prepared by heating dimethyl-

indigotin with *p*-toluidine and boric acid, crystallises in dark blue needles with a copper reflex. Chromic acid oxidises it to *o*-methylisatin, and nitric acid to the red 7:7'-dimethyldehydroindigotin-*p*-toluidide tetranitrate.

E. F. A.

Indigotin. III. 5:7:5':7'-Tetrabromoindigotin. Eugène GRANDMOUGIN (*Ber.*, 1909, 42, 4408—4411).—Tetrabromoindigotin is best prepared by brominating indigotin with 8 atoms of bromine in boiling nitrobenzene; it crystallises in lustrous copper crystals. The solubility depends largely on the purity of the product; it forms a blue solution in concentrated sulphuric acid. On oxidation in the cold with nitric acid, 5:7-dibromoisatin is formed; distillation with potassium hydroxide gives rise to 2:4-dibromoaniline. The constitution is there-



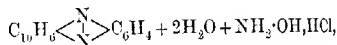
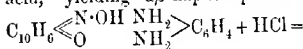
fore established (annexed formula).

On successive bromination of indigotin, 5:5'-dibromo-, 5:7:5'-tribromo-, and 5:7:5':7'-tetrabromo-derivatives are formed; on further bromination the halogen probably enters the positions 4:4'.

The leuco-compound of tetrabromoindigotin is readily obtained on reduction in alcoholic suspension with sodium hydrogen sulphite. This dissolves in alkalis with a yellow coloration, and dyes cotton yarn fast blue shades.

E. F. A.

Preparation of Azines from Nitroso- β -naphthols and *o*-Phenylenediamine. FRITZ ULLMANN and ROBERT HEISLER (*Ber.*, 1909, 42, 4263—4268).—*o*-Nitroso- β -naphthol, reacting as the tautomeric naphthaquinoneoxime, condenses with a boiling acetic acid solution of *o*-phenylenediamine in the presence of dilute hydrochloric acid, yielding $\alpha\beta$ -naphthaphenazine (Witt, *Abstr.*, 1887, 591):



which can be isolated by fractional precipitation with water. It is crystalline, and has m. p. 142°. A by-product formed during the reaction is 2:3-diaminophenazine (Griess, *J. pr. Chem.*, 1871, [ii], 3, 142; Fischer and Hepp, *Abstr.*, 1889, 499).

9-Hydroxynaphthaphenazine (Kehrmann and Brunnel, *Abstr.*, 1908, i, 579) can be obtained from 7-hydroxy- β -naphthaquinoneoxime (Clausius, *Abstr.*, 1890, 627) and *o*-phenylenediamine, or even better from the zinc salt of the nitrosonaphthol. Its *acetyl* derivative, $\text{C}_{18}\text{H}_{12}\text{O}_2\text{N}_2$, crystallises in brownish-yellow needles, m. p. 207°. The *methyl ether*, $\text{C}_{17}\text{H}_{12}\text{ON}_2$, forms glistening, yellowish-brown needles, m. p. 168°, and yields solutions with a green fluorescence.

Naphthaphenazine-5-carboxylic acid, $\text{C}_{16}\text{N}_2\text{H}_5\text{CO}_2\text{H}$, obtained from 1-nitroso-2:3-hydroxynaphthoic acid (Kostauecki, *Abstr.*, 1894, i, 91) and *o*-phenylenediamine, forms yellow needles, and when heated forms $\alpha\beta$ -naphthaphenazine. The *sodium* salt, $\text{C}_{17}\text{H}_5\text{O}_2\text{N}_2\text{Na}$, forms yellow, glistening needles. *Naphthaphenazine-8-sulphonic acid*,

$C_{16}H_{10}O_3N_2S$, obtained from 1-nitroso-2-naphthol-8-sulphonic acid (Meldola, *Trans.*, 1880, 39, 41) and *o*-phenylenediamine, crystallises in orange-yellow needles. The barium salt, $Ba(C_{16}H_9O_3N_2S)_2$, forms a red precipitate.

7-Acetylmino-naphthaphenazine, $C_{16}H_9N_3 \cdot NHAc$, from 1-nitroso-5-acetylmino-2-naphthol and *o*-phenylenediamine without the aid of hydrochloric acid, crystallises in pale yellow, felted needles, m. p. 311–313°, and when hydrolysed with sulphuric acid yields 7-amino-naphthaphenazine, $C_{16}H_{11}N_3$, as glistening, reddish-brown needles, m. p. 270–271°. J. J. S.

Function of the Nitrogen Atoms in Primary Hydrazines.

MAX BUSCH (*Ber.*, 1909, 42, 4596–4602).—A continuation of the investigations of the author and his co-workers on the interaction of primary hydrazines with carbimides and thiocarbimides (compare *Abstr.*, 1901, i, 234; 1903, i, 537; 1904, i, 628). It has been shown (*loc. cit.*) that $\beta\delta$ -dialkylthiosemicarbazides are formed by the interaction of hydrazines and thiocarbimides in cold alcohol, whereas $\alpha\delta$ -dialkylthiosemicarbazides are produced at higher temperatures or when the components are allowed to interact in the absence of a solvent; it would appear therefore that the amine in cold alcohol is present as an ammonium base, $NHR \cdot NH_2 \cdot OH$, in consequence of which it does not form a $\beta\delta$ -dialkylthiosemicarbazide, owing to the saturated character of the β -nitrogen atom. This view is supported by the following observations: (1) $\beta\delta$ -Diphenylthiosemicarbazide is formed by the interaction of phenylhydrazine and phenylthiocarbimide in alcohol, even at a high temperature, provided an acid, such as acetic or hydrochloric, is present. (2) The product of the reaction when the components are dissolved in benzene or ether, even at a low temperature, contains about 70% of $\alpha\delta$ -diphenylthiosemicarbazide.

Phenylcarbimide behaves like its sulphur analogue, but exhibits a greater tendency to combine with the β -nitrogen atom of the hydrazine.

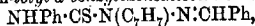
The course of the reaction in the case of aliphylhydrazines is not altered by the presence of an acid; thus, methylhydrazine sulphate and benzylhydrazine hydrochloride react with phenylthiocarbimide in alcoholic-acetic acid solution, yielding $\beta\delta$ -dialkylthiosemicarbazides.

$\beta\delta$ -Diphenylthiosemicarbazide hydrochloride, $C_{18}H_{13}N_3S \cdot HCl$, crystallises in small aggregates of microscopic leaflets, softens at 160°, m. p. 170° (decomp.). W. H. G.

Addition of Thiocarbimides to Ring-substituted Arylhydrazines. MAX BUSCH and JOHANNES REINHARDT (*Ber.*, 1909, 42, 4602–4610).—Contrary to the statement of Marekwald (*Abstr.*, 1897, i, 503), arylhydrazines containing substituents in the ortho-, meta-, or para-positions combine with thiocarbimides in alcoholic solution, particularly in the presence of acetic acid at a low temperature yielding $\beta\delta$ -dialkylthiosemicarbazides, which are fairly stable, passing into the $\alpha\delta$ -dialkyl isomerides when fused; in a few cases the $\beta\delta$ -derivatives have not been isolated owing to experimental difficulties.

δ -Phenyl- β -m-tolylthiosemicarbazide, $C_{14}H_{13}N_3S$, prepared from

m-tolylhydrazine and phenylthiocarbimide, crystallises in silvery, flat needles or leaflets, m. p. 132—133°, and condenses with benzaldehyde, yielding δ -phenyl- β -*m*-tolyl- α -benzylidenethiosemicarbazide,



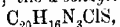
which crystallises in small, yellow nodules, m. p. 104°. The parent substance remains unchanged when treated with an alcoholic solution of hydrochloric acid, but passes into δ -phenyl- α -*m*-tolylthiosemicarbazide, $\text{C}_{14}\text{H}_{15}\text{N}_3\text{S}$, glistening, white leaflets, m. p. 156—157°, when heated for a short time at 135°.

δ -Tolyl- β -*m*-tolylthiosemicarbazide crystallises in colourless leaflets, m. p. 120—121°; the hydrochloride, $\text{C}_{15}\text{H}_{17}\text{N}_3\text{S} \cdot \text{HCl}$, forms white needles, m. p. 162°; δ -o-tolyl- α -*m*-tolylthiosemicarbazide forms granular aggregates of microscopic leaflets, m. p. 148°.

δ -p-Tolyl- β -*m*-tolylthiosemicarbazide forms glistening leaflets, m. p. 130—131°; the α -*m*-nitrobenzylidene derivative, $\text{C}_{22}\text{H}_{20}\text{O}_2\text{N}_3\text{S}$, crystallises in pale yellow needles or prisms, m. p. 198°; δ -p-tolyl- α -*m*-tolylthiosemicarbazide forms tufts of needles or rectangular prisms, m. p. 145—146°.

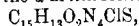
Methylthiocarbimide reacts with *m*-tolylhydrazine in the presence of glacial acetic acid, yielding a substance, crystallising in glistening, yellow prisms, m. p. 119—120°; an alcoholic solution of the components at 60° yields small quantities of a substance, crystallising in white prisms, m. p. 163°.

δ -Phenyl- β -*m*-chlorophenylthiosemicarbazide forms small, colourless, compact crystals, m. p. 117°; the α -benzylidene derivative,



crystallises in glistening, white leaflets or hexagonal plates, m. p. 146°; δ -phenyl- α -*m*-chlorophenylthiosemicarbazide has m. p. 153° (slight decomp.); Marckwald gives m. p. 138—139° (*loc. cit.*).

β -*m*-Chlorophenyl- δ -methylthiosemicarbazide crystallises in glistening, white needles, m. p. 105°; the α -*m*-nitrobenzylidene derivative,

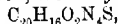


forms pale yellow needles, m. p. 224°; α -*m*-chlorophenyl- δ -methylthiosemicarbazide has m. p. 177°.

β -Phenyl- β -*m*-bromophenylthiosemicarbazide forms colourless crystals, m. p. 130°; the benzylidene derivative, $\text{C}_{20}\text{H}_{16}\text{N}_3\text{BrS}$, crystallises in glistening, yellow prisms, m. p. 164°; δ -phenyl- α -*m*-bromophenylthiosemicarbazide has m. p. 159—160°; the compound described by Marckwald (*loc. cit.*), m. p. 113°, is probably a mixture of the isomerides.

α -Bromophenyl- δ -methylthiosemicarbazide has m. p. 175° (decomp.) (Illgen gives m. p. 127—128°; *Diss.*, Berlin, 1894); a substance crystallising in tufts of white needles, m. p. 103°, is obtained by the action of methylthiocarbimide on *m*-bromophenylhydrazine in cold alcoholic solution; it is not an α -thiosemicarbazide.

δ -Phenyl- β -*m*-nitrophenylthiosemicarbazide forms aggregates of flat, pale yellow needles, m. p. 133°; the benzylidene derivative,



crystallises in pale yellow, matted needles, m. p. 165—166°.

δ -Phenyl- β -2-naphthylthiosemicarbazide, prepared by acting on β -naphthylhydrazine with phenylthiocarbimide in alcohol containing

acetic acid, crystallises in leaflets, m. p. 185°; the corresponding *δ*-methyl compound forms leaflets, m. p. 172° (decomp.); the benzylidene derivative of the former substance, $C_{24}H_{19}N_3S$, forms white leaflets, m. p. 206—207°.

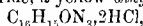
δ-Phenyl-*β*-o-tolylthiosemicarbazide crystallises in glistening, white leaflets, m. p. 124°.

δ-Phenyl-*β*-o-anisylthiosemicarbazide forms leaflets, m. p. 140—141°; the *m*-nitrobenzylidene derivative, $C_{21}H_{15}O_3N_3S$, crystallises in small, rectangular, yellow plates, m. p. 199—200°. W. H. G.

Isatinanils. I. Isatin-dimethylamino-2-anil. Its Formation, Hydrate, and Salts. RUDOLF FUMNER and MAX GOETTLER (*Ber.*, 1909, 42, 4269—4279).—Isatin-2-anils (*α*-isatinanilides) can be prepared by the condensation of aromatic nitroso-derivatives with indoxyllic acid in aqueous alcoholic solution. When nitrosobenzene and indoxyllic acid are used, isatin-2-anil, m. p. 125—126°, is obtained.

With *p*-nitrosodimethylaniline and indoxyllic acid in neutral or faintly acid solution at 15°, the chief product is a violet, crystalline powder, m. p. 105°, which yields isatin with sulphuric acid. Recrystallisation of the violet compound from 80% acetone converts it into *isatin-p-dimethylamino-2-anil*, $C_6H_4 \cdot \begin{smallmatrix} \text{NH} \\ \diagup \text{CO} \end{smallmatrix} \cdot C:N \cdot C_6H_4 \cdot NMe_2$,

which crystallises in intensely coloured prisms with a green, metallic lustre. It contains $1.5H_2O$, and has m. p. 183°. When powdered it has a green colour, but gives a red streak. When heated at 100° it loses its water of hydration and forms dichroic prisms with a metallic lustre, and then crystallises in bluish-red prisms, m. p. 182°. When the anil or its hydrate is shaken with an excess of an ethereal solution of hydrogen chloride, a yellow *dihydrate-chloride*,



m. p. 135—136°, is obtained, but when an excess of chloride is avoided, a *monohydrochloride*, $C_{16}H_{15}ON_3 \cdot HCl$, is formed; it crystallises in brilliant blue prisms with a violet lustre, and readily absorbs water. When heated to about 100°, an isomeric yellow *monohydrochloride* is formed, and from its brown aqueous solution isatin is gradually precipitated. The blue salt with chloroform or acetone also transforms into the yellow isomeride.

The *oxalate*, $C_{16}H_{15}ON_3 \cdot 1.5H_2C_2O_4$, crystallises in white needle-like prisms, m. p. 155°. The *picrate*, $2C_{16}H_{15}ON_3 \cdot C_6H_3N_3$, crystallises in bluish-black prisms, m. p. 179—180°.

When alkylated with sodium ethoxide and methyl iodide, the anil gives a *methyl derivative*, $C_{17}H_{17}ON_3$, which crystallises in lustrous, black plates, m. p. 125—126°, and yields 1-methylisatin on hydrolysis with hydrochloric acid.

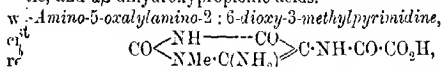
Acids readily decompose *p*-dimethylamino-2-anil into isatin and *p*-aminodimethylaniline salts, which react in the presence of sodium carbonate, yielding *isatin-p-dimethylamino-3-anil*, $C_{16}H_{15}ON_3$, m. p. 221—222°.

Violet-coloured dyes are formed when nitroso-compounds are condensed with indoxyllic acid in alkaline solution. J. J. S.

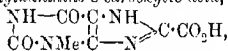
Preparation of 1-*p*-Dialkylaminophenyl-2:4-dimethyl-3-hydroxymethyl-5-pyrazolones. FARBWERKE FORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 214716).—The 1-*p*-dialkylaminophenyl-2:4-dimethyl-3-hydroxymethyl-5-pyrazolones are of therapeutic interest as being remarkably powerful antipyretics; they are produced by alkylating 1-*p*-aminophenyl-2:4-dimethyl-3-hydroxymethyl-5-pyrazolone with methyl iodide or methyl sulphate, the former methylation taking place in alcoholic solution. 1-*p*-Dimethylaminophenyl-2:4-dimethyl-3-hydroxymethyl-5-pyrazolone is a colourless, crystalline substance melting at 212°–213°. 1-*p*-Aminophenyl-2:4-dimethyl-3-hydroxymethyl-5-pyrazolone, colourless prisms, m. p. 249°, is produced by reducing 1-*p*-nitrophenyl-2:4-dimethyl-3-hydroxymethyl-5-pyrazolone, yellow crystals, m. p. 178–179°, the latter being obtained by condensing *p*-nitrophenylhydrazine and methyl acetoacetate to 1-*p*-nitrophenyl-3:4-dimethyl-5-pyrazolone, methylating this compound to 1-*p*-nitrophenyl-2:3:4-trimethyl-5-pyrazolone, yellow needles, m. p. 132°, brominating to 1-*p*-nitrophenyl-2:4-dimethyl-3-bromomethyl-5-pyrazolone, m. p. 213–214°, then treating this substance with alkali acetate in glacial acetic acid, whereby the bromine is replaced by hydroxyl, yielding 1-*p*-nitrophenyl-2:4-dimethyl-3-hydroxymethyl-5-pyrazolone acetate, yellow crystals, m. p. 163–164°, which, on hydrolysis with dilute sulphuric acid, gives the nitro alcohol.

F. M. G. M.

Preparation of Xanthine and Guanine Derivatives containing Substituents in Position 8. FARBENFABRIKEN TOUM. FRIEDRICH BAYER & Co. (D.R.-P. 213711).—The *o*-diaminopyrimidines, $\text{Y} \cdot \text{C} \begin{smallmatrix} \text{---} \text{NX} \text{---} \text{CO} \\ \text{---} \text{NX} \cdot \text{C}(\text{NH}_2) \end{smallmatrix} \text{C} \cdot \text{NH}_2$, yield formyl, acetyl, and propionyl derivatives, which, when heated, undergo further condensation to furnish xanthine and guanine compounds. This reaction has been generalised, with the result that the following acids can be employed for the condensation: oxalic, succinic, cyanoacetic, glycollic, lactic, hydantoic, hydroxyisobutyric, hippuric, acetylglycollic, ethoxy- and methoxy-tic, and $\alpha\beta$ -dihydroxypropionic acids.

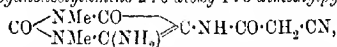


† obtained by condensing, at 160–170°, 4:5-diamino-2:6-dioxy-3-methylpyrimidine and fused oxalic acid; it crystallises with $1\frac{1}{2}\text{H}_2\text{O}$, and gives a disodium salt, which, on heating at 150–160°, yields the sodium salt of 3-methylxanthine-8-carboxylic acid,



the free acid of which crystallises with $1\frac{1}{2}\text{H}_2\text{O}$, and at 160° gives rise to 3-methylxanthine.

4-Amino-5-cyanoacetyl-amino-2:6-dioxy-1:3-dimethylpyrimidine,

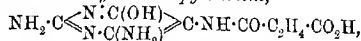


acicular crystals, is obtained by heating, at 120–130°, 4:5-diamino-2:6-dioxy-1:3-dimethylpyrimidine with cyanoacetic acid.

Theophylline-8-acetic acid, $\text{NMe} \cdot \text{CO} \cdot \text{C} \begin{smallmatrix} \text{NH} \\ \text{N} \end{smallmatrix} \begin{smallmatrix} \text{CO} \cdot \text{NMe} \cdot \text{C} \\ \text{N} \end{smallmatrix} \text{CH}_2 \cdot \text{CO}_2\text{H}$, is produced by heating the foregoing compound with aqueous sodium hydroxide until ammonia is completely evolved; it separates from water in aggregates of white needles.

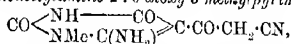
Ethyl theophylline-8-acetate, prepared by passing hydrogen chloride into the foregoing compound suspended in alcohol, forms crystals, melting at 215° .

2:4-Diamino-5-succinylamino-6-pyrimidone,

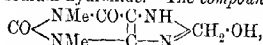


prepared from 2:4:5-triamino-6-pyrimidone and succinic acid, gives rise to succinylguaninepropionic acid and the hydrochloride of ethyl guaninepropionate, $\text{HCl} \cdot \text{NH}_2 \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{C}(\text{OH}) \cdot \text{C} \cdot \text{NH} \\ \text{N} \quad \quad \quad \text{C} \quad \quad \quad \text{N} \end{smallmatrix} \text{C}_2\text{H}_4 \cdot \text{CO}_2\text{Et}$.

4-Amino-5-cyanoacetylaminio-2:6-dioxy-3-methylpyrimidine,



prepared from 4:5-diamino-2:6-dioxy-3-methylpyrimidine and cyanoacetic acid, furnishes 3-methylxanthine-8-acetic acid on heating with excess of aqueous sodium hydroxide. The compound,



m. p. 240° , is obtained by heating 4:5-diamino-2:6-dioxy-1:3-dimethylpyrimidine and hydroxyacetic acid, and then warming the first condensation product with concentrated aqueous barium hydroxide.

The patent contains examples of several other condensation products of similar type containing lactyl, succinyl, and acetyl groups.

F. M. G. M.

Hydrazo-compounds. IV. Reactions of Hydrazobenzene with Aliphatic Aldehydes and with Benzoyl Chloride BERNHOLD RASSOW and OTTO BAUMANN (*J. pr. Chem.*, 1909, [ii], 80, 511—518).—The investigations of Rassow and Lummerzheim (*Abstr.* 1901, i, 777) have been extended to other aldehydes.

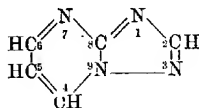
1:2:4:5-Tetraphenyl-3:6-diethylhexahydro-1:2:4:5-tetrazine

$\text{C}_6\text{H}_{13} \cdot \text{CH} \begin{smallmatrix} \text{NPh} \cdot \text{NPh} \\ \text{NPh} \cdot \text{NPh} \end{smallmatrix} \text{CH} \cdot \text{C}_6\text{H}_{13}$, m. p. 133° , is obtained by adding heptaldehyde to a hot solution of hydrazobenzene in 90% alcohol. Equal molecular quantities of hydrazobenzene and propaldehyde react with development of heat to form mainly propylidenebis(hydrazobenzene), $\text{NPh} \cdot \text{NPh} \cdot \text{CH} \cdot \text{Et} \cdot \text{NPh} \cdot \text{NPh}$, m. p. 153° . The minor product of the reaction, 3:6-diethylhexahydro-1:2:4:5-tetrazine, m. p. 193° , becomes the sole product when the aldehyde is added to hot 90% alcoholic hydrazobenzene.

Benzoylhydrazobenzene, $\text{NPhBz} \cdot \text{NPh}$, m. p. 136° , is obtained in 80% yield when an ethereal solution of hydrazobenzene and benzoyl chloride (2 mols.) is boiled with magnesium oxide; a second benzoyl group cannot be introduced.

C. S.

Synthetical Experiments on the Preparation of Derivatives of Hetero-condensed-heterocyclic "1:3-Triazo-7:0'-pyrimidine" [1:3:7:9-Benzotetrazole]. CARL BÜLOW and KARL HAAS (*Ber.*, 1909, 42, 4638—4644).—5-Amino-1:3:4-triazole (Thiele and Manchot, *Abstr.*, 1899, i, 168) condenses with 1:3-diketones in much the same manner as 1-amino-1:3:4-triazole (Bülow and Weber, *Abstr.*, 1909, i, 614, 615); two molecules of water are eliminated, and derivatives of "1:3-triazo-7:0'-pyrimidine" [1:3:7:9-



benztetrazole] (annexed formula) are formed.

When the 5-aminotriazole is condensed with ethyl acetoacetate and its homologues, 6- or 5:6-substituted derivatives of 4-hydroxy-1:3:7:9-benzotetrazole (heterohydroxylic acids) are obtained. The presence of the hydroxylic group imparts strongly acidic properties to the compounds, so that they yield neutral sodium salts, and can be titrated readily by means of standard alkali.

4:6-Dimethyl-1:3:7:9-benzotetrazole, $\begin{array}{c} \text{CMe}=\text{N}\cdot\text{C}\cdot\text{N} \\ \text{CH}\cdot\text{CMe}\cdot\text{N}\cdot\text{N} \end{array} > \text{CH}$, obtained by boiling an alcoholic solution of 5-amino-1:3:4-triazole with acetylacetone and a few drops of piperidine for fifteen hours, crystallises in colourless needles, m. p. 133°. It is readily volatile, it forms an unstable compound with nitric acid, and with silver nitrate an additive compound, $\text{C}_7\text{H}_5\text{N}_4\cdot\text{AgNO}_3$, which crystallises in short, stout needles.

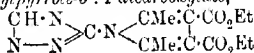
4:5:6-Trimethyl-1:3:7:9-benzotetrazole, $\text{C}_8\text{H}_{10}\text{N}_4$, obtained in a similar manner from methylacetylacetone, crystallises in colourless needles, m. p. 135—136°.

Benzoylacetone condenses slowly with 5-amino-1:3:4-triazole in glacial acetic acid solution, yielding tarry matter and 6-phenyl-4-methyl-1:3:7:9-benzotetrazole, $\text{C}_{12}\text{H}_{10}\text{N}_4$, which crystallises in needles, m. p. 134°.

4-Hydroxy-6-methyl-1:3:7:9-benzotetrazole, $\begin{array}{c} \text{CMe}=\text{N}-\text{C}\cdot\text{N} \\ \text{CH}\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{N} \end{array} > \text{CH}$, obtained by boiling for two hours a glacial acetic acid solution of 5-amino-1:3:4-triazole with ethyl acetoacetate, crystallises in colourless, glistening needles, m. p. 271° after sintering at 261°. A solution of the potassium salt gives amorphous precipitates with solutions of silver and copper salts. The mercuric, lead, zinc, barium, calcium, and cobalt salts have been obtained in crystalline forms.

4-Hydroxy-6-methyl-5-ethyl-1:3:7:9-benzotetrazole, $\text{C}_8\text{H}_{10}\text{ON}_4$, obtained from ethyl ethylacetoacetate and 5-methyl-1:3:4-triazole, crystallises in felted needles, m. p. 268° after sintering at 250°. Crystalline copper, cadmium, manganese, calcium, and magnesium salts have been prepared.

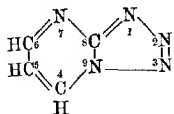
When a glacial acetic acid solution of ethyl diacetylsuccinate is boiled for four hours with the 5-aminotriazole, ethyl 1-(2':4':5')-triazolyl-2:5-dimethylpyrrole-3:4-dicarboxylate,



(compare Abstr., 1906, i, 906), is obtained. It crystallises from benzene and has m. p. 113°.

J. J. S.

Hetero-condensed, Heterocyclic Compounds with Two Nuclei: Substituted "Tetrazotopyrimidines." CARL BTLOW (*Ber.*, 1909, 42, 4429—4438).—*C*-Aminotetrazotic acid reacts with 1:3-diketones and with the esters of 1:3-ketocarboxylic acids similarly to 1-aminotriazole (Abstr., 1909, i, 614, 615), with production of derivatives of 1:2:3-tetrazoto-7:0'-pyrimidine [1:2:3:7:9-benzpentazole] (annexed formula). Condensation of aminotetrazotic



acid with acetylacetone yields 4:6-dimethyl-1:2:3:7:9-benzpentazole, which crystallises in long needles and has m. p. 150°. From methylacetylacetone, 4:5:6-trimethyl-1:2:3:7:9-benzpentazole, m. p. 123—125.5°, is obtained; it also crystallises in needles. 5-Phenyl-6-methyl-1:2:3:7:9-benzpentazole, prepared from benzoylacetone, forms white needles, m. p. 185°.

C-Aminotetrazotic acid condenses with ethyl acetoacetate, forming 4-hydroxy-6-methyl-1:2:3:7:9-benzpentazole, which crystallises in needles, and has m. p. 246—247°; it yields crystalline, mercurous, mercuric, lead, barium, iron, and strontium derivatives. 4-Hydroxy-6-phenyl-1:2:3:7:9-benzpentazole, prepared from ethyl benzoylacetate, forms white needles, m. p. 261° (decomp.). Both these compounds are strongly acidic, and may be titrated sharply with phenolphthalein; they are therefore to be regarded as heterohydroxylic acids (Abstr., 1909, i, 615).

By diazotising *C*-aminotetrazotic acid (Thiele, Abstr., 1892, 1299) and treating the product with acetoacetic ester, the azo-compound, ethyl tetrazolylazoacetate, $\begin{array}{c} \text{N} \\ | \\ \text{N} \text{---} \text{N} \\ | \quad | \\ \text{N} \text{---} \text{NH} \end{array} > \text{C} \text{---} \text{N} \text{---} \text{N} \text{---} \text{CHAc} \cdot \text{CO}_2\text{Et}$, is obtained; it forms yellow needles, m. p. 140—141°. The phenylhydrazone has m. p. 192—193°; on continued boiling with glacial acetic acid, it is converted into 4-tetrazolylazo-1-phenyl-3-methyl-5-pyrazolone, which has m. p. 201° (decomp.), and is apparently dimorphous (orange-yellow needles and deep red, compact crystals). R. V. S.

Preparation of a Soluble Double Compound of Theophylline and Piperazine. CHEMISCHE WERKE FORM. DR. HEINRICH BYK (D.R.-P. 214376).—Piperazine-theophylline is formed by combining molecular proportions of its components; it has an alkaline reaction, and is readily soluble in water, more sparingly so in alcohol.

F. M. G. M.

The Gelatinisation of Egg-Albumin by Hydrochloric Acid. I. GIOVANNI MORUZZI (*Biochem. Zeitsch.*, 1909, 22, 232—243).—The electrical conductivities and depression of freezing points of mixtures of egg-white solution and hydrochloric acid of concentrations $N=0$ to $N \times 0.692$ were determined, and compared with these physical constants for the same strengths in the absence of proteins. The degree of gelatinisation was noted in each case in the mixtures of

protein with acid. The maximum of $\Delta - \Delta'$ was noted when the normality of the acid reached 0.055, and remained about constant until the normality 0.554 was reached. In higher concentrations the value $\Delta - \Delta'$ was negative. The gelatinisation occurred between the concentration 0.103 and 0.244*N*. Experiments were also made to determine the changes of the viscosity of the mixtures during the process of gelatinisation, when the strength of acid = 0.018*N*. The electrical resistance and depression of freezing point remained constant during the time in which the viscosity increased. The change produced is apparently therefore neither molecular nor ionic, but probably due to a hydration of the colloid.

S. B. S.

The Hexone Bases from White of Egg. H. G. CHAPMAN and J. M. PETRIE (*J. Physiol.*, 1909, 39, 341—345).—By complete hydrolysis of 100 grams of egg-white with 25% sulphuric acid, the yield of hexone bases was as follows: arginine, 2.39; histidine, 0.66, and lysine, 3.19 grams.

W. D. H.

The Caseinogen-Peptones containing Phosphorus. M. DIETRICH (*Biochem. Zeitsch.*, 1909, 22, 120—130).—The products investigated were made by the peptic digestion of caseinogen, and isolated by Reh's method by means of precipitation by uranium salts. They were converted into calcium salts, which were separated into two fractions, one of which was insoluble on heating, and the other soluble. The former was dissolved in water, acidified with acetic acid, the solution neutralised, and from the solution thus obtained, other fractions were separated by means of copper, zinc, and lead salts. The fractions differed from one another in their readiness to yield inorganic phosphorus on hydrolysis. From the fractions of calcium salt which did not separate on heating, a peptone was separated by precipitation with uranyl acetate. The uranium precipitate was decomposed by hydroferrocyanic acid. The nitrogen and phosphorus were estimated in the various fractions. The caseinphosphoric acid isolated by means of the zinc salt was obtained in the largest quantity. It yielded, on hydrolysis, lysine, proline, and glutamic acid.

S. B. S.

Synthesis through Ferment Action. ALONZO E. TAYLOR (*Zeitsch. physikal. Chem.*, 1909, 69, 585—597. Compare *Abstr.*, 1909, ii, 344).—General remarks on the reversibility of enzyme reactions.

G. S.

Action of Proteolytic Enzymes on Protamines. M. TAKEMURA (*Zeitsch. physiol. Chem.*, 1909, 63, 201—214).—The following enzymes were found capable of acting on protamines in a weakly acid medium. Hedin's *lieu-β*-protease, Hahn and Geret's endotyptase, and papain. The action of pepsin is slight, and probably due to admixture with β -proteases.

W. D. H.

Reversibility of Enzyme Actions and the Effect of External Factors on Enzymes (Invertase, Maltase). FRIEDRICH G. KOHL (*Bied. Zentr.*, 1909, 38, 718; from *Beihft Bot. Centr.*, 1908,

23, i, 646—640).—Yeast extracts which were found to contain the largest amounts of invertase were allowed to act, in absence of light, on sucrose solutions of known strength at fixed temperatures, after excluding bacterial infection by means of thymol or chloroform. It was found that the dextrose and levulose increased for some time, after which the amounts generally remained stationary or the enzyme action was reversed. The time depended on the concentration and the temperature. Diffused daylight retards inversion, and 0.05% of asparagine quickens the hydrolysis. N. H. J. M.

Hydrolysis of Salicin by the Enzyme Emulsin. C. S. HUDSON and H. S. PAINE (*J. Amer. Chem. Soc.*, 1909, 31, 1242—1249).—The hydrolysis of salicin by strong acids has been shown by Noyes and Hall (*Abstr.*, 1896, ii, 159) to follow the law of unimolecular reactions. It has been stated by Henri, however, that the hydrolysis of the glucoside by emulsin does not take place in accordance with this law, and that the dextrose produced has $[\alpha]_D$ 52°.

Experiments have now been carried out which have given the following results. The dextrose formed by the action of emulsin on salicin is β -dextrose, $[\alpha]_D$ 20°. During the hydrolysis, the readings of the polarimeter are affected by the mutarotation of the dextrose, and this constituted a source of error in Henri's determinations. Measurements of the true rate of hydrolysis of salicin by emulsin at 0° and 30° have been made by rendering the solution slightly alkaline before determining its rotatory power. The results show that the rate follows the unimolecular order. Emulsin is only active in a nearly neutral solution, the activity being completely destroyed by sodium hydroxide of 0.005*N* and by hydrochloric acid of 0.014*N* concentration. E. G.

Influence of Acids on the Loss of Activity of Rennet Caused by Shaking. SIGNE SCHMIDT-NIELSEN and SIGVAL SCHMIDT-NIELSEN (*Zeitsch. physikal. Chem.*, 1909, 69, 547—556).—When a glycerol extract of rennet, diluted with water, is vigorously shaken in a tube, it rapidly loses its activity. The effect does not depend on the dissolving of alkali from glass, as it is also observed in quartz tubes.

In the quantitative experiments, the rennet solution was contained in a tube of Jena glass, and agitated by the up-and-down motion of an ebonite stirrer. The diminution of activity with the time of shaking does not follow any simple law; the rate of the diminution increases rapidly as the temperature is raised, but becomes less as the enzyme concentration is increased.

Acids, even in great dilution, lessen the rate of diminution of activity very considerably. Hydrochloric acid is most efficient in this respect; lactic, oxalic, and tartaric acids are about equally efficient, and acetic acid is least effective. The behaviour of sulphuric acid is remarkable, inasmuch as above a certain concentration further addition of acid has no action.

Commercial preparations of rennet are not affected by shaking, probably because they contain acids and neutral salts. G. S.

Chemical Composition and Biological Function of an Oxydase. HANS EULER and IVAR BOLIN (*Zeitsch. physikal. Chem.*, 1909, 69, 187—202).—The preparation of an oxydase from *Medicago sativa* is described. The fresh plants were comminuted, the juice pressed out, treated with alcohol, the precipitate redissolved, again precipitated by alcohol, and this process repeated several times. The product, in the form of a white powder, very soluble in water, was again dissolved in water, the solution boiled and filtered to remove proteins, the filtrate treated with charcoal, again filtered, precipitated with three times its volume of 96% alcohol, and the resulting powder dried in a vacuum. The preliminary treatment of the juice with alcohol may be omitted. The product, which showed all the properties of an oxydase, proved on analysis to consist of the neutral salts (mainly calcium salts) of certain polybasic organic acids, among which glycollic, mesoxalic, citric, malic, and probably glyoxylic acids have been detected. The acids were partly separated by fractional crystallisation of their barium salts.

Experiments on the accelerating influence of "laccase" and of salts of organic hydroxy-acids on the oxidation of polyphenols by free oxygen in the presence of manganese salts have already been described (compare Abstr., 1908, ii, 1031), and these experiments have now been extended. The rate of absorption of oxygen increases less rapidly than the manganese concentration, and also less rapidly than the concentration of the neutral salt of the oxyacid employed. The neutral salts of the different acids differ somewhat in catalytic power, but the effect is independent of the nature of the cation.

The physiological action of the oxydases is discussed. They do not effect the direct oxidation of sugars or fats. Sugar is partly broken down under the influence of enzymes, and the simpler compounds thus formed then undergo oxidation.

G. S.

Preparation of Derivatives of Phenylarsenious Oxide and of Arsenobenzene. FARBWERKE VORM MEISTER, LUCIUS and BRÜNING (D.R.-P. 212205. Compare Abstr., 1908, i, 591; 1909, i, 347).—2-Aminotolyl-5-arsenious oxide, $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{AsO}$, a white, crystalline powder, m. p. 160° , is prepared by reducing 4-amino-3-tolylarsinic acid in sulphuric acid solution by means of sulphurous acid in presence of potassium iodide.

Acetylaminocarboxyphenylarsenious oxide, $\text{NHAc}\cdot\text{C}_6\text{H}_3(\text{AsO})\cdot\text{CO}_2\text{H}$, a colourless powder, is prepared by boiling 2-acetylaminotolyl-5-arsinic acid during two hours with phenylhydrazine in methylic alcoholic solution.

o-Tolylglycine-5-arsinic acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{AsO}(\text{OH})_2$, m. p. 220° (decomp.), is prepared by treating 2-aminotolyl-5-arsinic acid with chloroacetic acid, and on reduction with sodium hyposulphite at 50° yields p-arseno-o-tolylglycine, a yellowish-brown powder, which blackens when heated above 200° . Arsenoacetylantiranic acid, a bright yellow powder, is prepared by reducing 2-acetylaminotolyl-5-arsinic acid with sodium hyposulphite in the presence of sodium acetate.

F. M. G. M.

Organic Chemistry.

Cuprous Compounds of Ethylene and of Carbon Monoxide. WILHELM MANCHOT and W. BRANDT (*Annalen*, 1909, 370, 286—296).—Manchot and Friend have shown (Abstr., 1908, ii, 375) that the combination of cuprous chloride with carbon monoxide depends on the formation of a compound, $\text{CuCl}\cdot\text{CO}\cdot 2\text{H}_2\text{O}$, or analogous substances containing ammonia, aniline, toluidine, etc., in place of water. It is now found that cuprous chloride and ethylene likewise combine, forming a dissociative compound in which one mol. of ethylene is united with 1CuCl ; the combination takes place, however, only in the presence of water, aniline, etc.; cuprous chloride does not form an additive product with dry ethylene, neither do these substances interact when dissolved in absolute alcohol.

All attempts to isolate the additive compound, which is far more soluble in water than cuprous chloride, have been unsuccessful, owing to the readiness with which it dissociates. Under identical conditions the ethylene compound is dissociated, as a general rule, to a far greater degree than the analogous carbon monoxide compound.

As in the case of the compounds of ferrous salts with nitric oxide (compare Manchot and Zechentmayer, Abstr., 1907, ii, 93), so also with the additive products of cuprous chloride with carbon monoxide and ethylene: when the concentration of the gas is kept constant the degree of dissociation is increased by raising the temperature.

W. H. G.

Specific Gravity of Solutions of Alcohols: Mixtures of Propyl Alcohol with Water. ANTONY G. DOROSCHEWSKY and M. S. ROSCHDESTVENSKY (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1428—1438).—The authors first discuss the literature concerning the specific gravity of propyl alcohol and its aqueous solutions. Their own experiments on the carefully purified and dehydrated alcohol give the value D_4^{20} 0.80804 and the conductivity 0.089×10^{-6} at 15° , those numbers not being altered by further distillation of the alcohol over calcium. The specific gravities of aqueous solutions containing from 0 to 100% of the alcohol were determined, the results being tabulated; the contractions for the various mixtures have been calculated.

T. H. P.

Stereochemical Isomerides of $\Delta\gamma$ -Hexin- β -diol. GEORGES DUPONT (*Compt. rend.*, 1909, 149, 1381—1383).— $\Delta\gamma$ -Hexin- β -diol, $\text{OH}\cdot\text{CHMe}\cdot\text{C}\equiv\text{C}\cdot\text{CHMe}\cdot\text{OH}$, has been described by Iotsitch (*Journ. Russ. Phys. Chem. Soc.*, 1903, 35, 430). When this compound is treated with bromine in chloroform solution, it yields a dibromide, m. p. 214 — 215° , mentioned by Iotsitch. The liquid from which this crystallises contains an isomeric dibromide, $\text{C}_6\text{H}_{10}\text{O}_2\text{Br}_2$, m. p. 119 — 120° . When treated with zinc dust and alcohol, these derivatives

VOL. XCVIII. i.

give two isomeric glycols: Iotsitch's compound, yielding crystals, m. p. 69—70°, b. p. 122°/15 mm., D_{13}^{20} 1.0205, n_D^{20} 1.4698, and forming a diacetyl derivative, m. p. 36°. The second glycol is a viscous liquid, b. p. 121°/15 mm., D_{13}^{20} 1.023, n_D^{20} 1.4733; the diacetyl derivative has m. p. 23—24°. Both glycols regenerate the corresponding dibromide when treated with bromine.

It follows, therefore, that the glycol prepared by Iotsitch is a mixture of these two isomerides. W. O. W.

Oxidation of Unsaturated Compounds with Organic Superoxides. NIKOLAUS PRILESCHAEFF (*Ber.*, 1909, 42, 4811—4815. Compare Gambarjan, *Abstr.*, 1909, i, 910).—Oxidation was carried out with benzoylhydroperoxide ($C_6H_5COO-OH$) dissolved in a neutral solvent at 0°, to which the calculated quantity of the unsaturated compound was added. The temperature is not allowed to rise above ordinary room temperature. The following oxides have been characterised.

Octylene oxide has b. p. 157—158°/740 mm., D_4^{20} 0.8395, D_4^{20} 0.8272, n_D^{20} 1.4165. On hydration, a glycol, b. p. 135—136°/20 mm., is obtained.

Diisobutylene oxide has b. p. 138—139°/765.5 mm., D_4^{20} 0.8418, D_4^{20} 0.8290, n_D^{20} 1.4157. It yields two glycols: *methylisooamylethylene glycol*, m. p. 60—61°, and *dimethyl-tert.-butylethylene glycol*, m. p. 64.5—65°.

Decylene oxide has b. p. 116—117°/50 mm., D_4^{20} 0.8465, D_4^{20} 0.8337, n_D^{20} 1.4275. The corresponding glycol has b. p. 151—152°/14 mm.

Propylene oxide, b. p. 162—163°/751 mm., D_4^{20} 1.1270, D_4^{20} 1.1136, n_D^{20} 1.4350. It does not yield glycerol on hydration, but forms a *hydroxychloroacetate*, b. p. 125—127°/17 mm.

Geraniol oxide has b. p. 157—158°/25 mm., D_4^{20} 0.9716, D_4^{20} 0.961, n_D^{20} 1.4681. A triol, b. p. 205—207°/20 mm., is formed on hydration.

Geraniol dioxide, formed when 2 mols. of benzoyl hydroperoxide are employed, has b. p. 180—183°/25 mm., D_4^{20} 1.0587, D_4^{20} 1.0472, n_D^{20} 1.4653. On hydration, a trioloxide, b. p. 220°/15 mm., m. p. 137—138°, is formed.

Linalool oxide has b. p. 95°/25 mm., D_4^{20} 0.9660, D_4^{20} 0.9507, $[\alpha]_D^{20}$ -4.38°, n_D^{20} 1.4554. It yields a doubly unsaturated aldehyde when hydrated, b. p. 120—122°/25 mm., D_4^{20} 0.8706, D_4^{20} 0.8573, n_D^{20} 1.5038, of which the semicarbazone has b. p. 138.5°.

Linalool dioxide has b. p. 131—133°/25 mm., D_4^{20} 1.0552, D_4^{20} 1.0423, $[\alpha]_D^{20}$ +5.34°, n_D^{20} 1.4616. It forms a trioloxide, b. p. 210—212°/25 mm., when hydrated.

Citral oxide has b. p. 146—148°/20 mm., D_4^{20} 1.0091, D_4^{20} 0.9740, n_D^{20} 1.4604, and gives a diolaldehyde, b. p. 141—142°/24 mm., D_4^{20} 1.0584, D_4^{20} 1.0335, when hydrated.

Citronellal oxide has b. p. 130—131°/25 mm., D_4^{20} 0.9437, D_4^{20} 0.9314, n_D^{20} 1.4421. On hydration, a diolaldehyde, b. p. 180—182°/18 mm., is formed.

Limonic oxide has b. p. 113—114°/50 mm., D_4^{20} 0.9435, D_4^{20} 0.9303, $[\alpha]_D^{20}$ -6.76°, n_D^{20} 1.4693, and yields a glycol, m. p. 66.5—67.5°.

Linylene dioxide has b. p. 146.5—147°/50 mm., D_4^{20} 1.0471,

$D_{15}^{25} 1.0338$, $[\alpha]_D +52.23^\circ$, $n_D^{16} 1.4702$. It forms an amorphous erythritol on oxidation, b. p. above $220^\circ/23$ mm.

Pinens oxide has b. p. $102-103^\circ/50$ mm., $D_0^{20} 0.9812$, $D_{15}^{20} 0.9689$, $[\alpha]_D -92^\circ$, $n_D^{15} 1.4708$; it is readily hydrated, forming *sobrerol*, m. p. 150° .

Aniline and 1 mol. of benzoylhydroperoxide form azobenzene; with 2 mols., nitrosobenzene is formed. In each case, a little nitrobenzene is formed. *o*-Toluidine gives *o*-nitrotoluene. E. F. A.

Results of Heating the Chlorides of the Higher Fatty Acids. AUGUSTIN BISTRZYCKI and AUGUST LANDTWING (*Ber.*, 1909, 42, 4720—4723).—The chlorides of the higher primary fatty acids do not lose carbon monoxide when heated (compare Abstr., 1908, i, 270), but it is now shown that they lose hydrogen chloride. Palmityl chloride, when heated at $250-275^\circ$ for four hours in a current of dry carbon dioxide, gives an almost theoretical yield of hydrogen chloride. From the residue a small amount of a product, *tris-tetradecylketen*, $(C_{16}H_{32}O)_3$, has been isolated, which crystallises from alcohol in plates. It softens at 60° , is completely molten at 72° , and is analogous to the compounds obtained by Wedekind and Haussermann (Abstr., 1908, i, 671) by the action of tertiary amines on acyl chlorides.

Lauryl chloride, under similar conditions, yields a *product*, $C_{12}H_{24}O$, m. p. $49-58^\circ$, and nonyl chloride, a solid product.

J. J. S.

α -Ethylpentenoic Acids and Xeronic Anhydride. FRITZ FICHTER and HANS OBLADEN (*Ber.*, 1909, 42, 4703—4707). Compare Fichter and Mueller, Abstr., 1906, i, 622).— γ -Methyl- α -ethylparaconic acid, $CO<\begin{smallmatrix} O-CHMe \\ CHEt \cdot CH \cdot CO_2H \end{smallmatrix}$, obtained by reducing

α -ethylacetylsuccinic ester with sodium amalgam and alcohol, has b. p. $192-196^\circ/12$ mm., and crystallises from a mixture of ether and light petroleum in colourless needles, m. p. 111° . When distilled slowly under atmospheric pressure, it yields unaltered acid, xeronic anhydride (Fittig, *Annalen*, 1887, 188, 59), and α -ethyl- Δ^2 -pentenoic acid, $CHMe:CH \cdot CHEt \cdot CO_2H$. The latter forms a gummy barium salt, has b. p. $116^\circ/12$ mm., and when boiled with 20% sodium hydroxide solution yields a mixture of α -ethyl- Δ^2 -pentenoic acid and unaltered Δ^2 -acid, the latter of which can be removed as α -ethylvalerolactone by treatment with 62% sulphuric acid (Young, Abstr., 1883, 455).

The Δ^2 -unsaturated acid has b. p. $120^\circ/12$ mm., and its barium salt, $(C_7H_{11}O_2)_2Ba \cdot H_2O$, crystallises in slender needles.

γ -Methyl- α -ethylitaconic acid, $CHMe:C(CO_2H) \cdot CHEt \cdot CO_2H$, is formed when xeronic anhydride, $O<\begin{smallmatrix} CO-CHEt \\ CO-CHEt \end{smallmatrix}$, is boiled with 20%

sodium hydroxide solution for twenty-four hours. The acid forms slender crystals, m. p. 136° , and yields an *anhydride*, $C_8H_{10}O_3$, as an oil, b. p. $142-144^\circ/12$ mm.

Xeronic anhydride and *p*-toluidine yield *xeronic-p-tolil*, needles, m. p. 107°. The isomeric *γ-methyl-α-ethylitacon-p-tolil* has m. p. 88° and b. p. 220°/12 mm. J. J. S.

β-Methylpentenoic Acids. FRITZ FICHTER and ERWIN GISSENER (*Ber.*, 1909, 42, 4707—4710).—A comparison of the dissociation constants of β-methyl-Δ^α-pentenoic acid and β-methyl-Δ^β-pentenoic acid shows that the Δ^α-unsaturated acid is the stronger acid; the values for *K* are Δ^α-acid, 0.00073, and Δ^β-acid, 0.00255 (compare Abstr., 1904, i, 965; 1906, i, 622). The Δ^β-acid was prepared by reducing α-methylacetylsuccinic ester (Bischoff, Abstr., 1881, 412) with sodium and aqueous alcohol to β-γ-dimethylparaconic acid, and distilling the latter slowly under atmospheric pressure. It was not found possible to isolate the isomeric Δ^α-acid from the mixture of acids obtained by boiling the Δ^β-acid with 10% sodium hydroxide solution, as both acids are converted by 62% sulphuric acid into β-methylvalerolactone (compare following abstract). The Δ^α-acid was therefore prepared by the elimination of hydrogen bromide from α-bromo-β-methyl-β-ethylpropionic acid.

β-Dimethylparaconic acid, $\text{CO} \begin{array}{c} \text{CH}_2 \cdot \text{CMe} \cdot \text{CO}_2\text{H} \\ | \\ \text{O} - \text{CHMe} \end{array}$ (50% yield), has b. p. 196°/9 mm., and crystallises in plates, m. p. 80°. The *ethyl ester* has b. p. 134°/10 mm. *β-Methyl-Δ^β-pentenoic acid*, $\text{CHMe} \cdot \text{CMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, has b. p. 96°/10 mm., or 199° under atmospheric pressure.

Ethyl α-bromo-β-methyl-γ-valerate, $\text{CH}_2\text{Me} \cdot \text{CHMe} \cdot \text{CHBr} \cdot \text{CO}_2\text{Et}$, obtained by brominating β-methylvaleric acid (Bentley, *Trans.*, 1895, 67, 264) by Auwers and Bernhardt's method (Abstr., 1891, 1189), using a Hirsch shaking apparatus, and subsequent treatment of the product with ethyl alcohol, has b. p. 91°/12 mm. When heated with quinoline, hydrogen bromide is eliminated and *ethyl β-methyl-Δ^α-pentenoate*, $\text{CH}_2\text{Me} \cdot \text{CMe} \cdot \text{CH} \cdot \text{CO}_2\text{Et}$, b. p. 176°, is formed. The corresponding *acid*, $\text{C}_6\text{H}_{10}\text{O}_2$, has m. p. 46° and b. p. 104°/12 mm., or 207° under atmospheric pressure. The *calcium salt*, $(\text{C}_6\text{H}_9\text{O}_2)_2\text{Ca} \cdot \text{H}_2\text{O}$, crystallises in brilliant plates, and the *zinc salt*, which also contains $1\text{H}_2\text{O}$, in needles.

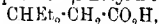
The formation of the isomeric Δ^α-unsaturated acid by the removal of hydrogen bromide from the brominated ester was not observed (compare Rupe, Ronus, and Lotz, Abstr., 1903, i, 139). J. J. S.

Remarkable Transformation of β-Dialkylated Acrylic Acids when Boiled with Sulphuric Acid. FRITZ FICHTER, ALBERT KIEFER, and WALTER BERNOLLI (*Ber.*, 1909, 42, 4710—4713).—Fittig's statement (Abstr., 1891, i, 204) that Δ^α-unsaturated acids are transformed into the isomeric lactones when heated with 62% sulphuric acid, whereas the Δ^β-unsaturated acids are unaffected, is not without exceptions (compare Blaise and Luttringer, Abstr., 1905, i, 168). It is shown that β-methyl-Δ^α-pentenoic acid (preceding abstract) is quantitatively transformed into β-methylvalerolactone when heated with 62% sulphuric acid. Under similar conditions, β-ethyl-Δ^α-pentenoic acid yields β-ethylvalerolactone.

Ethyl isopentylmalonate, $\text{CH}_3\text{Et}_2\text{CH}(\text{CO}_2\text{Et})_2$, obtained from γ -iodopentane and sodiumethylmalonate, has b. p. $130^\circ/16$ mm. The acid, $\text{C}_8\text{H}_{14}\text{O}_4$, has m. p. 58° , and yields a sodium hydrogen salt,



in the form of colourless plates. *β -Ethyl- n -valeric acid*,



has b. p. 212° . *Ethyl α -bromo- β -ethyl- n -valerate*, $\text{CH}_3\text{Et}_2\text{CHBr}\cdot\text{CO}_2\text{Et}$, has b. p. $165^\circ/25$ mm., and with quinoline yields *ethyl β -ethyl- Δ^a -pentenoate*, $\text{CH}_3\text{Et}_2\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, which has b. p. 187 — 188° . The acid, $\text{C}_8\text{H}_{13}\text{O}_4\text{Br}$, has b. p. 217 — 218° , and the *toluidide*, $\text{C}_{14}\text{H}_{19}\text{ON}$, has m. p. 35° and b. p. 210 — $215^\circ/15$ mm. J. J. S.

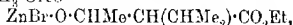
Decomposition of Crotonic Acid by Heating with Ammonia.

FRITZ FICHTER and HANS P. LADHARDT (*Ber.*, 1909, 42, 4714—4715. Compare Engel, Abstr., 1888, 1063).—When crotonic acid is heated with the compound $\text{CaCl}_2\cdot 8\text{NH}_3$ for eight to ten hours at 225 — 230° , the chief product is 2-methyl-5-ethylpyridine (Auerbach, Abstr., 1893, i, 175). The formation of this compound is to be attributed to the decomposition of the crotonic acid into acetaldehyde and acetic acid, and the condensation of the former to aldehydecollidine.

[With ALBERT KIEFER.]—Dimethylacrylic acid under similar conditions yields *s*-trimethylpyridine. J. J. S.

Synthesis of β -Hydroxy- α -isopropylbutyric Acid. I. MATZURE-

VITSCH (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1319—1324).—The action of zinc on a mixture of acetaldehyde and ethyl α -bromo- β -methylbutyrate (α -bromoisovalerate) proceeds according to the equations: (1) $\text{CHMe}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{Et} + \text{Zn} = \text{CHMe}_2\cdot\text{CH}(\text{ZnBr})\cdot\text{CO}_2\text{Et}$; (2) $\text{CHMe}_2\cdot\text{CH}(\text{ZnBr})\cdot\text{CO}_2\text{Et} + \text{CH}_3\cdot\text{CHO} =$

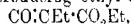


and the latter $+ \text{H}_2\text{O} = \text{OH}\cdot\text{CHMe}\cdot\text{CHPr}^{\beta}\cdot\text{CO}_2\text{Et} + \text{ZnBr}\cdot\text{OH}$.

Ethyl β -hydroxy- α -isopropylbutyrate, $\text{OH}\cdot\text{CHMe}\cdot\text{CHPr}^{\beta}\cdot\text{CO}_2\text{Et}$, best prepared in presence of benzene, is a yellow, mobile liquid with a faint, pleasant odour, b. p. 111.5 — $114^\circ/38$ — 37 mm., D_4^{20} 0.97182, n_D^{20} 1.43296; it gives the normal molecular weight in boiling ether. The corresponding acid was obtained as an almost colourless liquid; the sodium, potassium, and barium salts were prepared and analysed.

T. H. P.

Ketens. XIV. Ethyl Ethylketencarboxylate. HERMANN STAUDINGER and ST. BEREZA (*Ber.*, 1909, 42, 4908—4918. Compare this vol., i, 46).—An ethereal solution of ethyl bromoethylmalonate chloride reacts with zinc, producing ethyl ethylketencarboxylate,

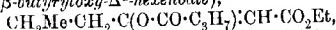


which rapidly polymerises, forming, with 80% yield, 1:3-diethylcyclobutan-2:4-dione-1:3-dicarboxylate, $\text{CO}_2\text{Et}\cdot\text{CEt}\cdot\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix}\cdot\text{CEt}\cdot\text{CO}_2\text{Et}$, which distils in a high vacuum at 113 — 116° as a colourless oil. With aniline it yields ethyl ethylmalopauilate. When heated in an oil-bath at 180 — 200° , it is depolymerised, and the unimolecular keten passes over. *Ethyl ethylketencarboxylate* so prepared is a colour-

less liquid, b. p. 48°/15 mm., m. p. 57·86°. It has the characteristic properties, not of a ketoketen, but of an aldoketen. It is probable that all ketens form bimolecular polymerides, which are cyclobutane derivatives. The bimolecular polymeride of keten itself is probably not an acetylketen (compare Chick and Wilsmore, *Trans.*, 1908, 93, 946), but Δ^1 -cyclobuten-1-ol-3-one, $\text{CO} \begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH} \end{smallmatrix} \text{C} \cdot \text{OH}$.

Ethyl ethylmalonate chloride, obtained from the ester-acid by means of phosphorus pentachloride, has b. p. 75—77°/13 mm. It yields an anilide, m. p. 55—56°. *Ethyl bromoethylmalonate chloride*, prepared from the above chloride by the action of bromine in hot carbon disulphide solution, has b. p. 95—102°/14 mm. R. V. S.

Action of Ethyl Bromoacetate and Zinc on the Anhydrides of Monobasic Acids. ANDREAS LUNIAK (*Ber.*, 1909, 42, 4808—4811).—By the interaction of molecular quantities of ethyl bromoacetate and acid anhydrides, C-diacyl compounds are obtained. Thus acetic anhydride yielded ethyl- α -acetylacetoacetate, isolated as the copper salt, m. p. 149°. From propionic anhydride the copper salt of *ethyl dipropionylacetate* was obtained, crystallising in dark violet crystals, which turned greyish-green at 84° (corr.), m. p. 98° to a dark green liquid. *Ethyl dipropionylacetate* is a colourless liquid of characteristic odour, b. p. 120·5—121·5°/20 mm., D_4^{20} 1·0527. The copper salt of *ethyl dibutrylacetate* forms a bright violet precipitate of thin prisms; it becomes greyish-green at 89° (corr.), m. p. 98°. *Ethyl dibutrylacetate* is a colourless liquid, b. p. 139—140°/24 mm., D_4^{20} 1·0168, and shows a dark red coloration with ferric chloride. *Ethyl O-butyryl-butyrylacetate* (β -butyryloxy- Δ^3 -hexenoate),



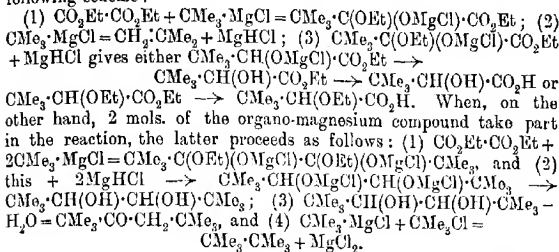
has a characteristic fruity odour, b. p. 137—137·5°/12 mm., D_4^{20} 0·9956, and shows no ferric chloride coloration. E. F. A.

Action of Magnesium *tert*-Butyl Chloride on Ethyl Oxalate. MILLE V. I. EGOROVA (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1454—1463).—In syntheses of alcohols by means of organo-magnesium compounds, just as in syntheses effected with organo-zinc derivatives, the reactions may proceed in two directions, according to the conditions. One of these conditions is the temperature, the raising of which promotes reduction, and another, which is not possessed by aromatic radicles, the more or less marked reducing properties of the radicle combined with the magnesium (compare Bouveault, *Abstr.*, 1904, i, 546; Sabatier and Mailhe, *Abstr.*, 1905, i, 706; Letellier, *Abstr.*, 1908, i, 242). With ethyl oxalate and magnesium *tert*-butyl chloride, as was to be expected, the reaction follows an abnormal course, owing to the pronounced reducing properties of the Grignard compound. In order that both the ethoxy-groups of the ethyl oxalate may react, to 1 mol. of the oxalate must be taken 4 mols. of magnesium *tert*-butyl chloride, 2 mols. for the introduction of the radicles, and two for forming the 2 mols. of magnesium hydrogen chloride necessary for the reduction.

The reaction gives rise to the following products: (1) isobutylene;

(2) *a*-hydroxy- $\beta\beta$ -dimethylbutyric acid, $\text{CMe}_3\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, which forms rectangular plates, m. p. $87-88^\circ$; (3) *a*-ethoxy- $\beta\beta$ -dimethylbutyric acid, $\text{CMe}_3\cdot\text{CH}(\text{OEt})\cdot\text{CO}_2\text{H}$, m. p. 121° , the calcium salt of which is more soluble in cold than in hot water; (4) the ethyl ester of another acid, formed only in small quantity; (5) the ketone, $\text{CMe}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CMe}_3$, which is a colourless liquid, b. p. $152.5-154.5^\circ$, with a camphor-like odour, and is probably formed by the dehydration, by the alcoholic potassium hydroxide employed for hydrolysis, of part of (6) the glycol, $\text{CMe}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CMe}_3$, m. p. $90-92^\circ$, b. p. $120-130^\circ/33\text{ mm.}$, which has a camphor-like odour; (7) hexamethylethane.

The formation of these various products is explained by the following scheme:



T. H. P.

Production of Traces of Formaldehyde in the Oxidation of Ethyl Alcohol by Chemical, Physical, or Biological Methods. E. VOISENET (*Compt. rend.*, 1910, 150, 40-43).—Advantage has been taken of the coloration developed by formaldehyde in a solution of albumin containing nitrous acid, to test for this substance in the products of oxidation of pure alcohol (*Abstr.*, 1906, ii, 59). Definite proof of the presence of formaldehyde was obtained whether the oxidation was effected by the chromic acid mixture, by electrolysis, by contact with finely divided metals, or through the agency of micro-organisms.

W. O. W.

A New Cupric Salt and its Application as a Fungicide for Diseases of the Vine and Other Plants. PHILIPPE MALVEZIN (*Bull. Soc. chim.*, 1909, [iv], 5, 1096-1098).—When cupric hydroxide, or copper hydrogen carbonate, is suspended in a 40% aqueous solution of formaldehyde, and sulphur dioxide is passed through the mixture, a deep blue solution is formed. This contains the substance represented by the formula: $\text{Cu}(\text{SO}_3\cdot\text{CH}_2\cdot\text{OH})_2$, which it is proposed to call cupric diformaldisulphite. The following is suggested as the method of formation of this product: $\text{CH}_2\text{O} \longrightarrow \text{CH}_2(\text{OH})_2 \longrightarrow \text{OH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{SO}_3\text{H} \longrightarrow \text{Cu}(\text{SO}_3\cdot\text{CH}_2\cdot\text{OH})_2$. The advantages in practice of this substance as a fungicide over "Bordeaux mixture" and other cupric products are described.

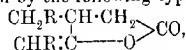
T. A. H.

Catalytic Hydrogenation of Unsaturated Organic Compounds. H. FOURNIER (*Bull. Soc. chim.*, 1910, [iv], 7, 23—27).—The substance to be reduced is placed in a flask containing platinum-black, and communicating with a supply of hydrogen. Sometimes it is advantageous to dissolve the substance in ether. The mixture is kept continuously agitated, and the action continued until hydrogen is no longer absorbed. The catalytic activity of the platinum may be restored when necessary by heating the metal for a few minutes at 200—220°.

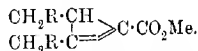
Under these conditions crotonaldehyde furnishes *n*-butyraldehyde and *n*-butyl alcohol, *isosafole* and *safrole* give dihydro*isosafole*, and *eugenol* and *isoeugenol* yield dihydro*eugenol* [propyl*guaiaacol*] (compare Delange, *Bull. Soc. chim.*, 1908, [iv], 3, 505, and Parrain, *Abstr.*, 1907, i, 43). T. A. H.

Conversion of *iso*Butyl Alcohol into α -Methylglyceraldehyde. SIMON ZEISEL and M. DANIEK (*Monatsh.*, 1909, 30, 727—728. Compare Vignier, *Abstr.*, 1909, i, 691).—*iso*Butyl alcohol was converted into *isobutaldehyde*, and this by means of bromine in presence of marble transformed into the *methylacetal* of α -*bromoisobutaldehyde*. Potassium hydroxide at high temperatures converted this into the *methylacetal* of α -methylacraldehyde, from which, by means of potassium permanganate, α -methylglyceraldehyde *methylacetal* was obtained and converted into the free aldehyde. E. F. A.

Preparation and Description of Condensation Products of Sodium Derivatives of the Acyloins (Hydroxyketones) with Esters of the Acetic Series. LOUIS BOUVEAULT and RENÉ LOECQX (*Bull. Soc. chim.*, 1909, [iv], 5, 1136—1144).—An extension of a paper already published (*Abstr.*, 1907, i, 479), giving details of the methods of preparation used, descriptions of compounds prepared by the general reaction, and in some cases additional data regarding substances described already. It is now proposed to represent the condensation products of this reaction by the following typical formula:



whilst the esters from them are to be represented by that formerly proposed (*loc. cit.*):



The reasons for the adoption of these formulæ are as follows. The condensation products are (1) only feebly acid, (2) form dibromides, and (3) are readily attacked by oxidising agents, giving 1 mol. each of a fatty acid and a substituted succinic anhydride, (4) the esters formed from them are reduced by sodium in alcohol to homologues of *cyclopropanecarbinol*, so that they must contain a trimethylene ring and a double linking in the $\alpha\beta$ -position with respect to the carboxyl group.

The condensation products were prepared as already described (*loc. cit.*). They gave small yields of esters when esterified by the usual methods, and recourse was therefore had to the use of

diazomethane for this purpose. In this way yields of about 80% of the theoretical were obtained.

The product $\begin{array}{c} \text{CHEt} \cdot \text{CH} \cdot \text{CH}_2 \\ \text{CHMe} \cdot \text{C} \longrightarrow \text{O} \end{array} > \text{CO}$, b. p. 190—195°/12 mm., obtained from propion, is liquid at the ordinary temperature, and cannot be obtained crystalline (*loc. cit.*).

The corresponding substance, $\text{C}_{10}\text{H}_{16}\text{O}_2$, b. p. 210—215°/20 mm., m. p. 116°, obtained from butyrolin, crystallises from boiling water; it furnishes an *amide*, m. p. 63—64°, and yields an *ethyl ester*, $\text{C}_{12}\text{H}_{20}\text{O}_2$, b. p. 160°/18 mm. (approx.), and a *methyl ester*, b. p. 143—148°/10 mm. The latter on reduction furnishes *dipropylcyclopropanecarbinol*, b. p. 96—98°/8 mm. or 104—105°/12 mm., which has a mint-like odour, and yields an *acetate* having the same boiling point as itself, and a *pyruvate*, l. p. 125°/8 mm. (approx.), of which the *semicarbazone* has m. p. 97—98°.

*iso*Butyrolin under the same conditions yields a *product*, $\text{C}_{10}\text{H}_{16}\text{O}_2$, b. p. 200—210°/25 mm., which crystallises in part.

Hexonoin yields a substance, $\text{C}_{11}\text{H}_{24}\text{O}_2$, b. p. 250—260°/20 mm. and m. p. 100—111° (*loc. cit.*), which on keeping decomposes spontaneously, yielding valeric acid and a second acid, possibly amylsuccinic acid. The methyl ester from this condensation product has b. p. 205°/19 mm. (*loc. cit.*).

T. A. H.

Effect of Negative Substituents on the Formation of Semicarbazones. HANS RUPE and SIDONIUS KESSLER (*Ber.*, 1909, 42, 4715—4720. Compare this vol., i, 15).—The influence of negative groupings (Rupe and Metz, *Abstr.*, 1903, i, 535) on semicarbazone formation is shown in the following reactions. β -Bromoisobutyl methyl ketone, $\text{CMe}_2\text{Br} \cdot \text{CH}_2 \cdot \text{COMe}$, forms a semicarbazone readily, mesityl oxide dibromide, $\text{CMe}_2\text{Br} \cdot \text{CHBr} \cdot \text{COMe}$, with difficulty, and bromomesityl oxide, $\text{CMe}_2\text{CBr} \cdot \text{COMe}$, does not form a semicarbazone.

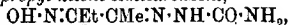
Aliphatic oximino-ketones react with semicarbazide, yielding semicarbazones, and with excess of the carbazide the oximino-group is eliminated and bis-semicarbazones are formed. Oximino-derivatives of the aromatic series react but slowly with semicarbazide, or, in some cases, do not react at all.

Methyl β -bromoisobutyl ketone, $\text{C}_5\text{H}_{11}\text{OBr}$, obtained by the addition of hydrogen bromide to mesityl oxide, is a clear, colourless oil, b. p. 52—53°/11 mm., and when kept, even in the absence of air, forms a dark-coloured syrup. The *semicarbazone*,

$\text{CMe}_2\text{Br} \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, crystallises in slender, colourless needles, m. p. 113° (decomp.).

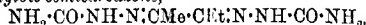
Mesityl oxide dibromide (Claisen, this Journ., 1876, i, 985), obtained by passing a current of carbon dioxide saturated with bromine vapour into mesityl oxide cooled with ether and solid carbon dioxide, yields a *semicarbazone*, $\text{C}_7\text{H}_{13}\text{ON}_3\text{Br}_2$, which crystallises in pale yellow, glistening needles, m. p. 290—295°.

Oximinoacetone-semicarbazone, $\text{OH} \cdot \text{N} \cdot \text{CH} \cdot \text{CMe} \cdot \text{N} \cdot \text{HN} \cdot \text{CO} \cdot \text{NH}_2$, forms small, colourless, pointed needles, m. p. 218° (decomp.), and yields an *acetyl derivative*, $\text{C}_8\text{H}_{10}\text{O}_3\text{N}_4$.

Oximinomethyl propyl ketone-semicarbazone,

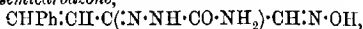
forms a crystalline powder, m. p. 228°, and yields an *acetyl* derivative, $\text{C}_8\text{H}_{14}\text{O}_3\text{N}_4$, m. p. 207°.

Pyruvaldehydebis-semicarbazone, $\text{C}_5\text{H}_{10}\text{O}_2\text{N}_4$, obtained by the action of an excess of semicarbazide hydrochloride on oximinacetone, crystallises in slender, lustreless needles, m. p. 254—255° (decomp.).

Acetylpropionylbis-semicarbazone,

obtained from oximinomethyl propyl ketone, has m. p. 250°.

Oximinobenzylidenacetone reacts in the course of several weeks with an aqueous alcoholic solution of semicarbazide, yielding a small amount of a *semicarbazone*,



m. p. 197° (decomp.).

A bis-semicarbazone could not be obtained.

J. J. S.

Electrolysis of Dextrose, Glycerol, and Glycol. WALTHER LÖB [in part with G. PULVERMACHER] (*Zeitsch. Elektrochem.*, 1910, 16, 1—9).—A solution containing from 20 to 60% of dextrose and 5% of sulphuric acid was placed in a porous pot containing a spiral of lead tubing, which was cooled with water and served as anode. The current density was about 0.05 ampere per sq. cm., and the temperature about 16°. The electrolysis was stopped when a comparatively small quantity of the dextrose was oxidised. The changes which occur are interpreted thus: dextrose is first hydrolysed to arabinose and formaldehyde. Dextrose itself is oxidised to gluconic and saccharic acids, arabinose to arabonic and trihydroxyglutaric acids, and formaldehyde to formic acid and carbon monoxide and dioxide. The non-volatile acids were not identified with certainty, as they were separated in the form of a mixture of their calcium salts. When the lead coil is used as cathode instead of anode, the greater part of the dextrose is reduced to mannitol, but formaldehyde and a pentose (yielding an osazone, m. p. 170—172°), were also present in small quantities.

L-Arabinose, when oxidised in the same way as dextrose, yields formaldehyde and a sugar, from which a tetrose has not yet been isolated.

Glycerol yields considerable quantities of formaldehyde and a pentose (probably *D*-arabinose). It is probable that glyceraldehyde is the first product of the oxidation; this is hydrolysed into glycolaldehyde and formaldehyde, and the glycolaldehyde and glyceraldehyde then condense to a pentose. Formic acid is the only volatile acid present, and the non-volatile acids are probably tartronic and trihydroxyglutaric acids, formed by oxidation of glycerol and the pentose respectively. The oxidation of ethylene glycol, under the conditions used for the other substances, yields formaldehyde, formic acid, and carbon dioxide, and minute quantities of a sugar and a non-volatile acid which is not glycollic acid. The sugar was not a pentose, and contained neither dihydroxyacetone, glyceraldehyde, nor glycolaldehyde. It gave an osazone melting at 184—185°, and was probably a hexose. T. E.

The Scission of Sugars. VII. The Reversal of the Sugar Synthesis. WALTHER LÖB and GEORG PULVERMACHER (*Biochem. Zeitsch.*, 1909, 23, 10—26).—The authors have investigated the action of lead hydroxide and sodium hydroxide on sugar solutions under varying conditions. They have isolated formaldehyde, pentose, acetylcarbinol, acetylmethylcarbinol, formic acid, polyhydroxy-acids, and possibly pentitol. Their main conclusions are: the sugar synthesis is a reversible one; formaldehyde and pentose are phases in sugar scission and sugar synthesis; the scission of dextrose into formaldehyde and pentose takes place in solutions, the alkalinity of which corresponds with that of the blood; the reaction also takes place in acid solutions when, owing to oxidation or reduction, the original equilibrium has been disturbed; as shown by the electrolysis of ethylene glycol and glycerol, a sugar synthesis also takes place in acid solutions, from the aldehydes which are then formed by the scission of the sugars.

S. B. S.

Kinetic Studies in the Sugar Series. EMIL VOTOČEK and H. NĚMEČEK (*Zeitsch. Zuckerind. Böhm.*, 1910, 34, 237—248; *Sitzungsber. böhm. Akad. Wissens.*, 1908).—The rate of action of bromine-water on the aldoses is considerably influenced by their configuration; galactose, for example, is much more rapidly oxidised than dextrose. Lævulose is not acted on by bromine water of low concentration.

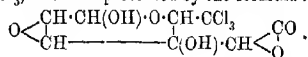
The oxidation of aldoses by bromine water is retarded by hydrochloric, hydrobromic, and sulphuric acids.

Dextrose and galactose are both oxidised at the ordinary temperature, being converted quantitatively into gluconic and galactonic acids, and it is probable that the other aldehydic sugars behave in a similar manner.

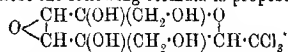
Aldoses can be distinguished from ketoses by means of the reaction with bromine water.

N. H. J. M.

Choraloses. MAURICE HANRIOT (*Ann. Chim. Phys.*, 1909, [viii], 18, 466—502). A résumé of information, most of which has been published already; chloralose (Abstr., 1893, i, 247; 1894, i, 105); arabinochloralose and xylochloralose (Abstr., 1895, i, 321); galactochloralose and lævulochloralose (Abstr., 1896, i, 519); chloralic acids (Abstr., 1909, i, 206, 287) (compare also Heffter, Abstr., 1889, 845, and Petit and Polonowsky, Abstr., 1894, i, 394). *Mannochloralose*, m. p. 208°, yields an *acetyl* derivative, m. p. 163°, crystallising in large, colourless needles, and a *benzoyl* derivative, m. p. 152°. Mannochloralac lactone, $C_8H_7O_6Cl_3$, is best represented by the formula:



For lævulochloralose the following formula is proposed:



Dibenzoylarabinochloralose has b. p. 275°. Arabinobromalose, prepared like the chloral compound, has m. p. 210°, and occurs in small, indefinite crystals.

The chloralic acids from β -chloralose and xylochloralose are identical, and the crystals are monoclinic [$a:b:c=1.500:1:2.628$; $\gamma=83^\circ$]. Similarly, the chloralic acids from galactochloralose and arabinochloralose are identical (the crystals are rhombic: $a:b:c=1.319:1:0.825$). Manno-chloralic acid is not isomeric with the other acids of this group. A discussion of isomerism among the chloraloses and their derivatives is given.

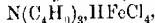
T. A. H.

The Contraction Occurring when Sucrose is Dissolved in Water. G. FOUQUER (*Bull. Assoc. chim. Sucr. Dist.*, 1909, 27, 545—549. Compare Abstr., 1908, i, 855).—In reply to statements that contraction does not take place when sucrose is dissolved in water, the author points out that the values determined indirectly for the contraction depend on the density of the sugar dissolved, sucrose having been found to have the two values D 1.5881 and D 1.61. The contraction occurring when a concentrated sugar solution is diluted may be observed by placing about 200 c.c. of the solution in a 500 c.c. flask, and adding water at the same temperature up to the mark, taking care that the two mix as little as possible. On now mixing the water with the sugar solution by rotating the flask, a marked contraction of the total volume will be noticed. The author also shows that in dilute solutions the contraction is approximately proportional to the concentration.

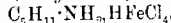
W. P. S.

Iron Double Salts of Organic Bases. MAX SCHOETZ (*Arch. Pharm.*, 1909, 247, 534—541).—The chlorides of almost all of the metals except iron have been frequently utilised in preparing double chlorides for the characterisation of organic bases. The ferrichlorides are very soluble in water, but are precipitated by concentrated hydrochloric acid as well crystallised compounds of constant composition. The solution of the organic base in the least possible quantity of dilute hydrochloric acid is treated with an excess of ferric chloride, and the mixture is treated slowly with fuming hydrochloric acid until it becomes turbid; after a short time, the crystalline ferrichloride separates. In the case of many aromatic amines, the method is inapplicable, since the hydrochloride of the amine is less soluble than the ferrichloride, and is therefore precipitated first.

The following new ferrichlorides are mentioned (compare Abstr., 1908, i, 202): *diethylamine ferrichloride*, $\text{NHEt}_2 \cdot \text{HFeCl}_4$, m. p. 128° , greenish-yellow prisms; *triethylamine ferrichloride*, $\text{NEt}_3 \cdot \text{HFeCl}_4$, hygroscopic, greenish-yellow needles; *tetraethylammonium ferrichloride*, $(\text{NEt}_4)\text{FeCl}_4$, groups of light yellow needles, sintering above 240° ; *methyltripropylammonium ferrichloride*, $(\text{NMePr}_3)\text{FeCl}_4$, m. p. 80° , yellow, rhombic crystals; *tributylamine ferrichloride*,

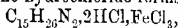


m. p. 171° , yellow needles; *amylamine ferrichloride*,

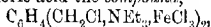


yellow needles; *diamylamine ferrichloride*, $\text{NH}(\text{C}_5\text{H}_{11})_2 \cdot \text{HFeCl}_4$, sinters and melts above 170° , yellow, crystalline powder; *triethylamine ferrichloride*, $\text{N}(\text{C}_2\text{H}_5)_3 \cdot \text{HFeCl}_4$, yellow needles; *dibenzylamine ferrichloride*, $\text{NH}(\text{C}_6\text{H}_5)_2 \cdot \text{HFeCl}_4$, m. p. 145° , yellow prisms; *methylpyridinium*

ferrichloride, $C_6H_5NMe_2FeCl_4$, yellow needles; *piperidine ferrichloride*, $C_3NH_{11}HFeCl_4$, m. p. 163° , yellow prisms; *benzylethylconinium ferrichloride*, like the iodide (Abstr., 1904, i, 1044), exists in two forms: the α -form has m. p. 92° and forms yellow needles; the β -form has m. p. 116° and crystallises in compact octahedra; *dibenzylconinium ferrichloride*, $C_6H_{13}N(C_2H_5)_2FeCl_4$, has m. p. 141° ; *tetrahydroquinoline ferrichloride*, $C_9NH_{11}HFeCl_4$, m. p. 144° , orange-red, rhombic crystals. The additive compound of tropine and benzyl chloride (Abstr., 1905, i, 79) forms a *ferrichloride*, $C_8H_{13}ON, C_2H_5Cl, FeCl_3$, m. p. 109° , orange-yellow needles. Sparteine hydrochloride forms a compound,



which sinters at 190° , and gradually decomposes. Sparteine methochloride forms the compound, $C_{17}H_{28}N_2, MeCl, HCl, FeCl_3$, yellow needles, decomposing above 240° . *o*-Xylylenedipyridinium chloride forms a compound, $C_6H_4(CH_2Cl, C_5NH_5, FeCl_3)_2$, m. p. 102° , yellow needles. The additive compound of *o*-xylylene bromide and triethylamine is converted by silver chloride into the chloride, which yields with ferric chloride and hydrochloric acid the compound,



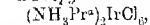
m. p. 80° , slender, yellow needles.

C. S.

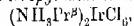
Hexahalogen-irideates. [Iridichlorides and Iridibromides.]

ALEXANDER GUTHRIE and M. RIESS (*Ber.*, 1903, 42, 4770—4777).—On adding a solution of a substituted ammonium bromide drop by drop to a solution of hydrogen iridichloride in dilute hydrochloric acid at the ordinary temperature, a precipitate of the corresponding substituted ammonium iridichloride is formed. If, however, the solution of hydrogen iridichloride is heated to boiling while the bromide is added, some hydrobromic acid being also present, it changes colour from a reddish-brown, through green, to a deep blue. The formation of the latter colour indicates the change from the iridichloride into the iridibromide. This change can also be brought about by digesting the iridichlorides with dilute hydrobromic acid. The crystals which separate on cooling are not pure, and must be recrystallised from a dilute solution of hydrobromic acid containing free bromine.

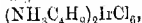
The following compounds are described: *Methylammonium iridichloride*, $(NH_2Me)_2IrCl_6$, brownish-red needles. *Dimethylammonium iridichloride*, $(NH_2Me)_3IrCl_6$, reddish-brown, rhombic crystals. *Trimethylammonium iridichloride*, $(NH_2Me)_4IrCl_6$, small needles. *Ethylammonium iridichloride*, $(NH_2Et)_2IrCl_6$, brownish-red plates. *Diethylammonium iridichloride*, $(NH_2Et)_3IrCl_6$, brownish-red needles. *Triethylammonium iridichloride*, $(NEt_3)_2IrCl_6$, small needles, which were not obtained pure. *n*-Propylammonium iridichloride,



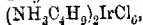
brownish-red needles. *iso*-Propylammonium iridichloride,



brownish-red needles. *n*-Butylammonium iridichloride,



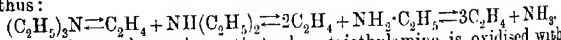
reddish-brown plates. *iso*-Butylammonium iridichloride,



brownish-red needles. *Ethylenediammonium iridichloride*,
 $(C_2H_5)_2N_2IrCl_6$
 brownish-red needles. *Propylenediammonium iridichloride*,
 $(C_3H_7)_2N_2IrCl_6$
 reddish-brown crystals. *Pyridinium iridichloride*, $(PyH)_2IrCl_6$ red.
 dish-brown needles. *α -Picolinium iridichloride*, $(C_5NH_3Me)_2IrCl_6$
 brownish-red needles. *Quinolinium iridichloride*, $(C_9NH_3)_2IrCl_6$
 black, monoclinic prisms, or brownish-red needles. *Benzylammonium*
iridichloride, $(C_6H_5\cdot NH_2)_2IrCl_6$, dark brownish-red plates.
Methylammonium iridibromide, $(NH_2Me)_2IrBr_6$, dark blue octa-
 hedra. *Dimethylammonium iridibromide*, $(NH_2Me)_2IrBr_6$, dark
 blue needles. *Trimethylammonium iridibromide*, $(NH_3Me)_2IrBr_6$,
 dark blue needles. *Ethylammonium iridibromide*, $(NH_3Et)_2IrBr_6$,
 dark blue plates. *Diethylammonium iridibromide*,
 $(NH_3Et_2)_2IrBr_6$,
 dark blue, monoclinic prisms. *Triethylammonium iridibromide*,
 $(NH_3Et_3)_2IrBr_6$,
 dark blue plates. *n-Propylammonium iridibromide*, $(NH_3Pr)_2IrBr_6$,
 dark blue, six-sided plates. *iso-Propylammonium iridibromide*,
 $(NH_3Pr^i)_2IrBr_6$,
 dark blue needles. *n-Butylammonium iridibromide*,
 $(NH_3\cdot C_4H_9)_2IrBr_6$,
 dark blue, six-sided plates. *iso-Butylammonium iridibromide*,
 $(NH_3\cdot C_4H_9^i)_2IrBr_6$,
 dark blue plates. *Ethylenediammonium iridibromide*, $(C_2H_5)_2N_2IrBr_6$,
 deep blue, cubical crystals. *Propylenediammonium iridibromide*,
 $(C_3H_7)_2N_2IrBr_6$,
 deep blue prisms. *Pyridinium iridibromide*, $(PyH)_2IrBr_6$, deep blue
 plates. *α -Picolinium iridibromide*, $(C_5NH_3Me)_2IrBr_6$, dark blue,
 six-sided, monoclinic plates. *Quinolinium iridibromide*,
 $(C_9NH_3)_2IrBr_6$,
 dark blue needles. *Benzylammonium iridibromide*, $(NH_3\cdot C_6H_5)_2IrBr_6$,
 dark blue, six-sided plates.

The substituted ammonium iridibromides are not so stable as the alkali iridibromides, and will not withstand prolonged exposure to light. In general, the bromo-salts of the platinum metals are very readily decomposed, both as such, and in solution. T. S. P.

Behaviour of Triethylamine towards Oxidising Agents.
 T. DAR JUAN (*Amer. Chem. J.*, 1910, 43, 1-6).—The oxidation of triethylamine may take place either by the direct union of oxygen to form the oxide, $Et_3N\cdot O$, and the subsequent oxidation of this compound to nitric and acetic acids, or by the conversion of the ethylidene groups into acetaldehyde, and the formation of ammonia. In accordance with Nef's view, the latter reaction would take place thus:



Experiments have shown that when triethylamine is oxidised with aqueous solution of potassium permanganate, the carbon residues are converted quantitatively into acetic acid, neither carbonic nor oxalic acid being produced, whilst the nitrogen appears partly as ammonia and partly as nitric acid.

In presence of potassium hydroxide, acetic acid is the chief oxidation product, but oxalic and carbonic acids are also produced. Nitric acid and ammonia are both formed, but the latter is produced in much larger quantity in this case than in the absence of alkali hydroxide.

E. G.

Methylated Guanidines. MARTIN SCHENCK (*Arch. Pharm.*, 1909, 247, 466—490).—Numerous attempts to prepare methylated guanidines by the interaction of guanidine and methyl iodide in methyl alcohol have given unsatisfactory results; the reaction does not proceed to any extent, and usually gives complicated mixtures. However, methylguanidine, $\text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{NHMe}$, and *s*-dimethylguanidine have been isolated as the platinichlorides.

Methyl sulphate and dry guanidine sulphate do not react at the ordinary temperature, or on the water-bath, but at $150\text{--}160^\circ$ the reaction leads to the formation of *s*-dimethylguanidine and a trimethylguanidine (*aurichloride*, m. p. $155\text{--}156^\circ$; *platinichloride*, m. p. $225\text{--}226^\circ$), which is shown to be the symmetrical compound, $\text{NMe}\cdot\text{C}(\text{NHMe})_2$, by comparison with a sample obtained by the interaction of *s*-dimethylthiocarbamide, excess of 10% alcoholic methylamine, and mercuric oxide on the water-bath.

The interaction of methyl iodide and the silver derivative of guanidine (prepared by Thiele's method, and also by that of Kutscher and Otori) in methyl alcohol on the water-bath is again unsatisfactory; methylguanidine and *s*-dimethylguanidine have been isolated as the platinichlorides, but the products are mainly mixtures. The author finds that the silver derivative of guanidine, prepared by the methods mentioned, always shows a deficiency of silver.

The methylguanidines obtained by the oxidation of creatine, or of methylglycoeyamidine, by the interaction of methylamine and cyanamide, and those isolated from meat extract and urine are all one and the same substance, $\text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{NHMe}$ (*aurichloride*, m. p. $198\text{--}200^\circ$, yellow needles; *platinichloride*, m. p. $194\text{--}195^\circ$, orange-red plates).

C. S.

Some Guanidine Derivatives. MARTIN SCHENCK (*Arch. Pharm.*, 1909, 247, 490—506).—Erlenmeyer showed that cyanamide is an intermediate product in the formation of guanidine from cyanogen chloride and alcoholic ammonia. Cyanamide has hitherto not been detected as an intermediate product in the reaction between cyanogen iodide and alcoholic ammonia, but by allowing a mixture of the two to remain at the ordinary temperature for several days, the author has detected cyanamide in the reaction product in the form of its characteristic yellow silver derivative. The formation of guanidine, therefore, probably occurs thus: (1) $\text{NCl} + 2\text{NH}_3 = \text{NC}\cdot\text{NH}_2 + \text{NH}_4\text{I}$; (2) $\text{NC}\cdot\text{NH}_2 + \text{NH}_4\text{I} = (\text{NH}_2)_2\text{C}\cdot\text{NH}\cdot\text{HI}$. By a similar process, cyanogen iodide and 10% alcoholic methylamine (3 mols.), after being heated for several hours in a closed vessel in steam, yield *s*-dimethylguanidine, of which the platinichloride has m. p. 197° , and the aurichloride, 122° . Under the preceding conditions there is practically no reaction between cyanogen iodide and alcoholic dimethylamine. Ethylenedi-

amine ($\frac{1}{2}$ —1 mol.), however, yields ethyleneguanidine (2-imino-4-hydroxyglyoxaline), $\begin{matrix} \text{CH}_2\cdot\text{NH} \\ \text{CH}_2\cdot\text{NH} \end{matrix} > \text{C}:\text{NH}$, of which the *platinichloride*, $2\text{C}_2\text{H}_5\text{N}_3\cdot\text{H}_2\text{PtCl}_6$, decomposing at 190° , *picrate*, m. p. 219° , and *aurichloride*, $\text{C}_2\text{H}_5\text{N}_3\cdot\text{HAuCl}_4$, m. p. 210° , have been prepared. In a similar way, alcoholic propylenediamine (less than 1 mol.) and cyanogen iodide yield propyleneguanidine (2-imino-4-methyltetrahydroxyglyoxaline), $\begin{matrix} \text{CHMe}\cdot\text{NH} \\ \text{CH}_2\text{---NH} \end{matrix} > \text{C}:\text{NH}$, the *platinichloride* of which has m. p. 194 — 195° , and the *aurichloride*, m. p. 100° . Under the same conditions, cyanogen iodide and trimethylenediamine yield a solution from which a crystalline *platinichloride*, *aurichloride*, or *picrate* has not been obtained. Cyanogen iodide and alcoholic aniline, heated in steam for several hours, yield only *p*-iodoaniline (compare Rabe, *Ber.*, 1877, 10, 1717).

A guanidine derivative has not been obtained by the interaction of cyanogen iodide and glycine or its ethyl ester. C. S.

Glycinamide. MARTIN SCHENCK (*Arch. Pharm.*, 1909, 247, 506—515).—Glycinamide is best prepared by keeping a mixture of chloroacetamide and ten times the quantity of 30% ammonium hydroxide in a closed vessel for fourteen days; the excess of ammonia is removed by evaporation, by gently warming in a basin, and finally drying the hydrochloride in a desiccator. A solution of the free base is obtained by means of silver oxide. An alcoholic solution of glycinamide is obtained by keeping ethyl glycine and a large excess of 5% alcoholic ammonia in a closed vessel for two to three weeks, then filtering, and freeing the filtrate from the excess of ammonia by a current of dry purified air. A guanidine derivative could not be obtained by the interaction of the aqueous or alcoholic solution of glycinamide and cyanogen iodide either at the ordinary temperature or by heating (compare preceding abstract), owing to the decomposition of the glycinamide into ammonia and glycine. C. S.

New Synthesis of Amino-hydroxy-acids and of Piperidone Derivatives. EMIL FISCHER and GÉZA ZEMPLÉN (*Ber.*, 1909, 42, 4878—4892).—The authors show that many ordinary α -bromo-acids, for example, α -bromopropionic, α -bromoisovaleric, α -bromoisobutyric, α -bromodihydrocinamic, are converted to the extent of 70—90% into the hydroxy-acid by boiling their aqueous solutions with calcium carbonate. The reaction has also been applied in the following directions. α -Bromo- δ -*m*-nitrobenzoylaminovaleric acid (Abstr., 1909, i, 303), when boiled with water and calcium carbonate, yields 57% of crystalline calcium α -hydroxy- δ -*m*-nitrobenzoylaminovalerate, $\text{Ca}(\text{C}_{12}\text{H}_{12}\text{O}_6\text{N}_2)_2\cdot 4\text{H}_2\text{O}$, m. p. 80° in its water of crystallisation. The free acid is a yellow oil, which is hydrolysed by boiling barium hydroxide or 5*N*-hydrochloric acid (and subsequent treatment with silver oxide), yielding δ -amino- α -hydroxyvaleric acid, $\text{NH}_2\cdot(\text{CH}_2)_3\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, m. p. 188 — 191° (decomp., corr.), which does not form proline by

treatment with hydrochloric acid or a copper salt with copper oxide. It appears to be a general rule that aqueous solutions of α - and β , but not those of γ , δ , or ϵ , amino-acids yield copper salts by boiling with copper oxide. By esterifying δ -amino- α -hydroxyvaleric acid by methyl alcohol and hydrogen chloride, and dechlorinating the ester-hydrochloride by silver oxide, or better by heating the acid at 190° , the lactam, 3-hydroxy-2-piperidone, $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{CH}(\text{OH}) \\ \text{CH}_2 \cdots \text{CH}_2 \end{smallmatrix} \text{CH}_2$, m. p. $141\text{--}142^\circ$ (corr.), is obtained, which forms a *platinichloride*, m. p. 160° (decomp.). In a similar manner, by esterification with methyl alcohol and hydrogen chloride and subsequent treatment with silver oxide, δ -aminovaleric acid yields 2-piperidone, and *i*-ornithine yields 3-amino-2-piperidone, which forms a *hydrochloride*, $\text{C}_5\text{H}_{10}\text{ON}_2\text{HCl}$, sintering at 220° and melting completely at 250° (decomp.), *platinichloride*, $2\text{C}_5\text{H}_{10}\text{ON}_2\text{H}_2\text{PtCl}_6\text{H}_2\text{O}$, decomposing at $200\text{--}205^\circ$, *picrate*, m. p. $160\text{--}162^\circ$ (corr.), and is reconverted into ornithine by prolonged heating with 20% hydrochloric acid at 100° .

The following compounds are obtained from α -bromo- ϵ -benzoylamino-hexoic acid (Braun, Abstr., 1909, i, 229) by a similar series of reactions: *calcium* α -hydroxy- ϵ -benzoylaminohexoate, a white, crystalline powder; α -hydroxy- ϵ -benzoylaminohexoic acid, m. p. 108° (corr.); ϵ -amino- α -hydroxyhexoic acid, m. p. $225\text{--}230^\circ$ (decomp., corr.), which does not yield a compound analogous to hydroxypiperidone. C. S.

Catalytic Action of Amino-acids, Peptones, and Proteins in Effecting Certain Syntheses. HENRY D. DAKIN (*J. Biol. Chem.*, 1909, 7, 49—56).—Many condensations, possibly analogous to those occurring in living cells, may be brought about by the use of amino-acids, peptones, proteoses, or even proteins as catalysts. For example, furfuraldehyde when warmed with malonic acid does not undergo condensation, but if glycine or alanine is added, considerable amounts of furfuralacrylic acid are formed. Attempts, however, to bring about certain other types of condensation (for example, the aldol condensation, condensation between aldehydes and ketones, etc.) by the same means failed. W. D. H.

Molybdenum Cyanides. ARTHUR ROSENHEIM, ABRAHAM GARFUNKEL, and F. KOHN (*Zeitsch. anorg. Chem.*, 1909, 65, 166—177).—Potassium molybdenum cyanide, $\text{K}_2\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$ (Chilesotti, Abstr., 1905, i, 177), contains the only known stable complex ion with a higher co-ordination number than six, and as there is also some doubt as to the valency of the molybdenum, its investigation has been undertaken.

The titration of reduced molybdenum solutions with permanganate is not interfered with by the presence of cyanides if rapidly performed, and the quinquevalence of the molybdenum in these salts is confirmed. A solution containing oxidised molybdenum (Mo^{VI}), manganous salts, and cyanides, however, undergoes a change under the catalytic influence of light, the manganese being partly oxidised by the molybdenum, and the manganous salt of the complex molybdenum

cyanide being precipitated. An excess of permanganate is therefore gradually decolorised if the solutions are exposed to light. The reaction with ammoniacal silver nitrate also proves the molybdenum in $\text{Mo}(\text{CN})_8$ to be quinquevalent. This can only be brought into harmony with the facts by doubling the molecule, thus making the complex anion $\text{Mo}_2(\text{CN})_{16}$.

A reddish-violet complex salt, $4\text{KCN} \cdot \text{MoO}_2 \cdot 10\text{H}_2\text{O}$, was described by Heide and Hofmann (Abstr., 1896, ii, 605) containing quadrivalent molybdenum. The salts of this series become blue on dehydration.

They must contain the complex anion $\left[\text{Mo} \begin{smallmatrix} (\text{OH})_4 \\ (\text{CN})_4 \end{smallmatrix} \right]$, in accordance with which they are only formed in strongly alkaline solution. Evaporation with water converts them into blue salts, containing the

anion $\left[\text{Mo} \begin{smallmatrix} \text{O}_2 \\ (\text{CN})_4 \end{smallmatrix} \right] \cdot 2\text{H}_2\text{O}$ or $\left[\text{Mo} \begin{smallmatrix} \text{O}_2 \\ (\text{H}_2\text{O})_2 \\ (\text{CN})_4 \end{smallmatrix} \right]$. Alkali cyanides convert the

blue salts into the yellow series, $\text{R}_3\text{Mo}_2(\text{CN})_{16}$, oxidation taking place.

The manganese salt of the yellow series, $\text{Mn}_2\text{Mo}(\text{CN})_8 \cdot 8\text{H}_2\text{O}$, forms bright yellow, glistening leaflets. The *silveramine*,

nickelamine, $[\text{Ni}(\text{NH}_3)_4]_2\text{Mo}(\text{CN})_8 \cdot 8\text{H}_2\text{O}$, and *pyridinium*, $(\text{C}_5\text{NH}_5)_4\text{Mo}(\text{CN})_8$,

salts are also described. *Hydromolybdic acid*,

$\text{H}_4\text{Mo}(\text{CN})_8 \cdot 6\text{H}_2\text{O}$,

is prepared by adding hydrochloric acid, D 1.19, to a concentrated solution of the potassium salt, extracting the precipitate with absolute alcohol, and precipitating with ether in a freezing mixture. The ether oxonium salt is decomposed with water, and precipitated with hydrochloric acid.

The sodium salt of the red series, $\text{Na}_4[\text{MoO}_2(\text{CN})_4] \cdot 14\text{H}_2\text{O}$, contains 2 mols. of constitutional water. C. H. D.

Malonyldihydrazones and their Decomposition Products.
CARL BÜLOW and C. BOZENHARDT (Ber., 1909, 42, 4784—4802).—Analogous to the condensation of malonyldihydrazide with ethyl acetate to ethylmalonylbishydrazonacetate (Bülow, Abstr., 1908, i, 253), the condensation of a number of substituted esters of 1:3-ketocarboxylic acids has been studied.

The ethyl esters of methyl-, ethyl-, isopropyl-, and benzyl-acetoacetates readily condense with malonyldihydrazide to form compounds of the type: $\text{CH}_2(\text{CO} \cdot \text{NH} \cdot \text{N} : \text{CMe} \cdot \text{CHR} \cdot \text{CO}_2\text{Et})_2$.

In a similar manner, methyl- and ethyl-malonyldihydrazides react with unsubstituted ethyl acetoacetate to form products:

$\text{CHR}(\text{CO} \cdot \text{NH} \cdot \text{N} : \text{CMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et})_2$.

On the other hand, it was not found possible to prepare dihydrazones of the type: $\text{CHR}(\text{CO} \cdot \text{NH} \cdot \text{N} : \text{CMe} \cdot \text{CHR} \cdot \text{CO}_2\text{Et})_2$, nor could malonyldihydrazide be coupled with ethyldimethylacetoacetate to form:

$\text{CH}_2(\text{CO} \cdot \text{NH} \cdot \text{N} : \text{CMe} \cdot \text{CR}_2 \cdot \text{CO}_2\text{Et})_2$.

Apparently alkyl derivatives of this class must contain at least four symmetrically distributed hydrogen atoms.

Ethyl malonylbishydrazoacetate, when boiled with water loses a part of the ethyl acetate, and 3-methyl-5-pyrazolone and an insoluble compound, considered to be a polymeride of cyclomalonic acid hydrazide, $\text{CH}_2 < \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{NH} \end{smallmatrix}$ are formed. This is difficult to analyse, but forms hydrazine and malonic acid on hydrolysis, and may be synthesised from malonyldihydrazide by prolonged boiling with acetic acid.

Sodium acetate solution acts similarly to water towards ethyl malonylbishydrazoacetate. Phenylhydrazine decomposes it into malonyldihydrazide and 1-phenyl-3-methyl-5-pyrazolone, which is converted on boiling with ferric chloride into pyrazole-blue. Potassium hydroxide converts it into malonic acid and 3-methyl-5-pyrazolone. Acetic anhydride forms diacetyldimalonyldihydrazide; dilute sulphuric acid decomposes it into malonic acid and hydrazine. Benzaldehyde interacts, forming ethyl acetoacetate and bisbenzylidenemalonyldihydrazine.

Resorcinol and cold concentrated sulphuric acid convert it into malonic acid, hydrazine sulphate, and β -methylumbelliferone.

Ethyl malonylbishydrazoacetate when kept for four months in water at the ordinary temperature decomposes, forming ethyl 3-methyl-5-pyrazolone-4-isopropylencarboxylate, malonic acid, and polymeric cyclomalonyldihydrazide. The carboxylic acid when heated is converted into the δ -lactone of 5-hydroxy-3-methylpyrazole-4-isopropylencarboxylic acid (Abstr., 1908, i, 579), which may also be obtained on slowly heating ethyl malonylbishydrazoacetate in a metallic bath above 125° .

Polymeric cyclomalonyldihydrazide, $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_2$, is obtained as a grey, amorphous powder, m. p. $266-267^\circ$. It is hydrolysed by sodium hydroxide, concentrated sulphuric acid, or sodium acetate to hydrazine and malonic acid.

Ethyl malonylbishydrazomethylacetoacetate, prepared from malonyldihydrazide and ethyl methylacetoacetate, separates in crystals, m. p. $109-110^\circ$.

Ethyl malonylbishydrazoethylacetoacetate is a colourless, microcrystalline powder, m. p. $106-106.5^\circ$.

Ethyl malonylbishydrazoisobutylacetoacetate has m. p. $104-105^\circ$.

Ethyl malonylbishydrazobenzylacetoacetate forms colourless needles, m. p. $129-130^\circ$.

Ethyl malonylbishydrazoethylacetoacetate, prepared from malonyldihydrazide and ethyl oxalacetate, is obtained as a glistening mass of large, matted needles, m. p. 127° .

Ethyl monomethylmalonylbishydrazoacetate separates in colourless aggregates of snow-like crystals, m. p. $92-93^\circ$.

Ethyl monoethylmalonylbishydrazoacetate, prepared from monoethylmalonyldihydrazide and ethyl acetoacetate, crystallises in small, colourless needles, m. p. $104-104.5^\circ$.

Monoethylmalonyldihydrazide is obtained from ethyl monoethylmalonate and hydrazine hydrate in long, matted needles, m. p. 166° .

E. F. A.
i 2

Synthesis of Hexahydrocymene. [*p*-Methylpropylcyclohexane]. WLADIMIR A. SÁIRNOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1374—1375).—*p*-Tolylidimethylcarbinol, $C_6H_4Me \cdot CMe_2OH$, prepared by the action of magnesium methyl iodide on *p*-tolyl methyl ketone, is a colourless liquid with a marked odour, b. p. $105^\circ/15$ mm., D_4^{20} 0.9769, n_D^{20} 1.5162. When reduced by means of hydrogen in presence of nickel at 150° , it yields hexahydrocymene [*p*-methylpropylcyclohexane], $C_{10}H_{20}$, b. p. 170 — $172^\circ/755$ mm., D_4^{20} 0.7974, n_D^{20} 1.4380, which corresponds closely in properties with the menthane obtained by Zelinsky by the reduction of menthone by means of hydrogen in presence of nickel. The investigation is being continued.

T. H. P.

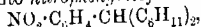
New Space Representation of the Benzene Molecule. JOHN C. EARL (*Chem. News*, 1909, 100, 305).—The representation in question consists of an octahedron with three sides removed, the remaining sides representing bonds linking the carbon atoms, the linking of the various carbon atoms being the same as in Ladenburg's prism formula. The formula represents satisfactorily the general behaviour of benzene and its derivatives. From it, theoretically only one mono-substitution product, one meta-di- and one para-di-substitution product, but two ortho-disubstitution products, can be formed, and di-, tetra-, and hexa-hydro-derivatives can exist without rupturing the ring.

G. S.

Presence of Ethylene Linkings in Benzene and its Homologues. K. W. CHARITSCHKOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1152—1154).—The oxidation of mesitylene by means of air in presence of powdered sodium hydroxide (compare Abstr., 1909, i, 134, 471) yields 1.17% of a monobasic acid, $C_9H_{11} \cdot CO_2H$, formed by the oxidation of one of the methyl groups. With *o*-, *m*-, and *p*-xylenes, under similar conditions, only very small proportions of acids are obtained. Hence, the degree of oxidisability of benzenoid hydrocarbons is independent of isomerism in the aromatic nucleus. This result, which is partly confirmed by the investigations on cymene and *p*-cymene, supports the conclusion that ethylene linkings are absent from benzene and its homologues, quite independently of the position of the substituent groups. These observations appear to give final confirmation to the diagonal structural formula for benzene and its homologues, which is supported by thermochemical data and by the action of reducing agents, such as hydrogen iodide, the reduction being accompanied by complete transformation of the six-membered ring into one containing five members. The author regards the supposed support given to the Kekulé formula by the action of ozone on benzene and its homologues as ill-founded, the compounds formed as the result of such action being peroxidic in character.

T. H. P.

Derivatives of Phenylidicyclohexylmethane. MARCEL GODCHOT (*Compt. rend.*, 1909, 149, 1137—1139).—When phenylidicyclohexylmethane (Abstr., 1909, i, 19) is dissolved in fuming nitric acid, it undergoes conversion into nitrophenylidicyclohexylmethane,

pale yellow needles, m. p. about 113° .

Phenyldicyclohexylcarbinol, $\text{CPh}(\text{C}_6\text{H}_{11})_2\cdot\text{OH}$, has been obtained by the action of ethyl benzoate on magnesium cyclohexyl bromide; it crystallises in prisms, m. p. 77° , and also with $1\frac{1}{2}$ mols. alcohol in prisms, m. p. 55° . Unlike triphenylcarbinol, it does not combine with aniline, phenol, or hydroxylamine. When distilled in a vacuum, the carbinol loses water, yielding a hydrocarbon, $\text{C}_6\text{H}_{11}\cdot\text{CPh}\cdot\text{C}_6\text{H}_5$. *Dinitrophenyldicyclohexylmethane*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{C}_6\text{H}_{11})_2\cdot\text{NO}_2$, m. p. 150° , arises from the action of fuming nitric acid on the foregoing carbinol, whilst under the same conditions the hydrocarbon yields a mononitro-derivative, m. p. 130° .

W. O. W.

Carbonium Perchlorates. KARL A. HOFMANN and HEINZ KIRMREUTHER (*Ber.*, 1909, 42, 4856—4865).—Coloured salts and molecular compounds of triphenylcarbinol and its derivatives have recently received much attention in connexion with the problem of colour and constitution, but hitherto salts of triphenylcarbinol and oxyacids have not been obtained in a crystalline form directly from their components. The authors find that perchloric acid yields beautifully crystalline derivatives with triphenylcarbinol, phenolphthalein, fluorescein, and distyryl ketone. The acid is a 71% solution, obtained by evaporating the commercial acid until the temperature is 136° and then distilling.

Hydrated triphenylmethyl perchlorate, $\text{CPh}_3\cdot\text{ClO}_4\cdot\text{H}_2\text{O}$, is obtained by adding 6 c.c. of 71.5% perchloric acid to an ethereal solution of 2 grams of the carbinol. It crystallises in deep yellow octahedra with a blue shimmer, and decomposes by heating or by the addition of water. Triphenylmethyl perchlorate, $\text{CPh}_3\cdot\text{ClO}_4$, obtained by the addition of 71% perchloric acid to a cold solution of the carbinol in acetic anhydride, crystallises in octahedra, which are brownish-yellow to brownish-red by transmitted light and blue by reflected light. The same substance is apparently produced when a mixture of perchloric acid and ethereal triphenylmethyl chloride is evaporated over sulphuric acid; when the evaporation is performed in an atmosphere of hydrogen chloride, citron-yellow octahedra with a blue lustre are obtained of a mixed salt, $2\text{CPh}_3\cdot\text{Cl}\cdot\text{CPh}_3\cdot\text{ClO}_4$.

Phenolphthalein perchlorate, $\text{C}_{20}\text{H}_{14}\text{O}_4\cdot\text{ClO}_4\cdot\text{H}_2\text{O}$, obtained from its components, forms dichroic crystals, which are ruby-red by transmitted and pale blue by reflected light; it is instantly decomposed by water. Fluorescein diperchlorate, $\text{C}_{20}\text{H}_{12}\text{O}_5\cdot 2\text{HClO}_4$, obtained in a similar manner, is a yellow powder.

[With H. LÉCHER.]—Distyryl ketone perchlorate, $\text{C}_{17}\text{H}_{14}\text{O}\cdot\text{HClO}_4$, is precipitated as a red powder by the addition of 71% perchloric acid to ethereal distyryl ketone. After being dried in a vacuum over phosphoric oxide, the substance is orange-red; it is instantly decomposed by water.

C. S.

Cryoscopy of Organic Mixtures and Additive Compounds. ABEL BUCQUET (*Compt. rend.*, 1909, 149, 857—858).—Additive compounds of acenaphthene with *a*-trinitrotoluene and 2:4-dinitrotoluene melt at 109° and 60° respectively, and the compound of phenanthrene with *a*-trinitrotoluene at 84° . Complete freezing-point curves of

mixtures of these hydrocarbons and their compounds take the form of a W, showing two eutectics and a maximum at the compound.

In the following cases, no compound being formed, the freezing-point curve is a V, showing one eutectic: phenanthrene with 2:4-dinitrotoluene and α -nitronaphthalene; acenaphthene with *p*-nitrotoluene; naphthalene with *p*-nitrotoluene, α -nitronaphthalene, acenaphthene, benzoic acid, salicylic acid, azobenzene, diphenylamine, guaiacol, chloral hydrate, menthol, methyl oxalate, phenanthrene, salol, and thymol.

R. J. C.

***p*-Hydroxyphenylethylamine.** KARL W. ROSENMUND (*Ber.*, 1909, 42, 4778—4783. Compare Barger, *Trans.*, 1909, 95, 1123, 2133).—

A relatively simple synthesis of *p*-hydroxyphenylethylamine is effected by condensing anisaldehyde with nitromethane to β -nitro-*p*-methoxystyrene, which can be directly reduced to *p*-methoxyphenylethylamine. It is preferable first to isolate the oxime of *p*-methoxyphenylacetaldehyde and reduce this to the amine. The methoxyl group is eliminated by boiling with decolorised hydriodic acid. The base is obtained by this method in good yield and in a pure state.

β -Nitro-*p*-methoxystyrene, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{NO}_2$, crystallises in long, yellow needles, m. p. 86—87°. It may be reduced with aluminium amalgam, or with zinc dust and acetic acid, to the oxime of *p*-methoxyphenylacetaldehyde, m. p. 120°, which is conveniently further reduced with sodium amalgam and alcoholic acetic acid. *p*-Methoxyphenylethylamine has a fish-like odour, b. p. 136—138°/18 mm. It forms a carbonate on exposure to the atmosphere. The hydrochloride has m. p. 207°.

p-Hydroxyphenylethylamine was obtained in glistening, colourless needles or plates, m. p. 160°; the hydroiodide forms yellow needles.

E. F. A.

Molecular Weights of Liquid Diphenylamine, Triphenylamine, and Aniline Hydrochloride. MARIE PRZYLUKSA (*J. China Phys.*, 1909, 7, 511—533. Compare Renard and Guye, *Abstr.*, 1907, ii, 334).—The surface-tensions of the three substances have been measured by Ramsay and Shield's method at a number of temperatures between their melting and boiling points. Diphenylamine distilled at atmospheric pressure gave irregular results, but after fractional distillation at 50 mm. pressure, the surface-tensions indicated a unimolecular constitution. The somewhat different conclusion arrived at by Dutoit and Friderich (*Abstr.*, 1900, ii, 194) may have been due to products of decomposition in their material.

Diphenylamine gives normal b. p. elevations in benzene or acetone, whereas Kahlenberg found it to be dissociated in acetonitrile. The surface-tension of diphenylamine indicates that its critical temperature would be 560° if it were not decomposed by heat.

Triphenylamine is polymerised to an increasing degree as the temperature rises from 108° to 335°, in agreement with the known tendency of such hydrocarbons to give condensation products on heating. Aniline hydrochloride passes directly at its boiling point (243°) from a polymerised liquid to a dissociated gaseous form.

R. J. C.

Action of Thiocarbimides on Alcohols and Mercaptans. I. New Method for Obtaining Mono-substituted Thio- and Dithiocarbamates of Monatomic Alcohols and Mercaptans. M. S. ROSCHDESTVENSKY (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1438—1454. Compare Abstr., 1909, i, 300).—Methyl phenylthiocarbamate, prepared by the action of sodium methoxide on phenylthiocarbimide, has m. p. 92.5—93.5° (Orndorff and Richmond, Abstr., 1900, i, 156, gave 97°). The corresponding ethyl derivative has m. p. 68—69° (Orndorff and Richmond, *loc. cit.*, gave 71—72°).

Allyl phenylthiocarbamate, $\text{NHPh}\cdot\text{CS}\cdot\text{O}\cdot\text{C}_3\text{H}_5$, forms aggregates of long needles, m. p. 64.5—65.5°; the *menthyl* ester,

$\text{NHPh}\cdot\text{CS}\cdot\text{O}\cdot\text{C}_{10}\text{H}_{19}$,
has m. p. 74—75°, $[\alpha]_D^{20} - 63.07^\circ$; the *benzyl* ester,

$\text{NHPh}\cdot\text{CS}\cdot\text{O}\cdot\text{CH}_2\text{Ph}$,

has m. p. 82—82.5°.

Methyl β -naphthylthiocarbamate, $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{CS}\cdot\text{OMe}$, prepared by the action of sodium methoxide on β -naphthylthiocarbimide, forms pale, cinnamon-coloured crystals, m. p. 104—105°. The *propyl* ester has m. p. 83—84°.

Methyl allylthiocarbamate, $\text{C}_3\text{H}_5\cdot\text{NH}\cdot\text{CS}\cdot\text{OMe}$, obtained by the action of sodium methoxide on allylthiocarbimide, is a brownish-yellow, mobile liquid with a peculiar odour, b. p. 121—122°/27 mm., $D_4^{20} 1.0811$, $D_4^{20} 1.0792$, $n_D^{20} 1.5379$; it combines readily with bromine, giving a crystalline product.

Bornyl allylthiocarbamate, $\text{C}_{10}\text{H}_{17}\cdot\text{NH}\cdot\text{CS}\cdot\text{O}\cdot\text{C}_3\text{H}_5$, forms white crystals, m. p. 59—60°, $[\alpha]_D^{20} + 14.25^\circ$.

Methyl phenyldithiocarbamate, $\text{NHPh}\cdot\text{CS}\cdot\text{SMe}$, prepared by the interaction of methyl mercaptan and phenylthiocarbimide in presence of sodium hydroxide, has m. p. 95—96° (compare Will, Abstr., 1882, 723; Losanitsch, Abstr., 1892, 55). The *ethyl* ester has m. p. 60—61° (Hofmann, *Ber.*, 1869, 2, 120, gave 56°, and Will, Abstr., 1882, 1088, gave 60°). The *propyl* ester,

$\text{NHPh}\cdot\text{CS}\cdot\text{SPr}^3$,

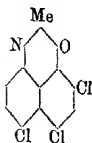
which may be prepared either in aqueous solution or in absence of water, has m. p. 66—67°.

Methyl β -naphthylthiodithiocarbamate, $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{CS}\cdot\text{SMe}$, has m. p. 116—117°.

T. H. P.

8-Amino-1-naphthol. II. FRITZ FICHTER and THEODOR KÜHNEL (*Ber.*, 1909, 42, 4748—4752. Compare Abstr., 1906, i, 839).—

Chlorine reacts with an acetone solution of 8-acetylamino-1-naphthol in much the same manner as bromine (*loc. cit.*, 840), yielding a crystalline precipitate of 6:7:9-trichloro-2-methylperinaphthoxazole (annexed formula) in the form of greenish-coloured needles, which do not melt below 300°.



8-Acetylamino-1-naphthoxyacetic acid,

$\text{NHAc}\cdot\text{C}_{10}\text{H}_7\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$,

obtained by condensing 8-acetylamino-1-naphthol with a concentrated aqueous solution of chloroacetic acid and potassium hydroxide, forms long, colourless needles, m. p. 245°. The *cupric* salt, $(\text{C}_{14}\text{H}_{12}\text{O}_4\text{N})_2\text{Cu}$,

forms slender, pale blue needles. When boiled with alkalis or acids, the acid does not yield a ring compound as the isomeric 1-acetyl-amino-2-naphthoxyacetic acid does (Spitzer, Abstr., 1901, i, 715).

The nitro-derivative obtained by the action of nitric acid on 8-acetylamino-1-naphthyl acetate is now shown to be the 5-nitro-derivative. This has been proved by hydrolysing the product to nitro-8-acetylamino-1-naphthol, the methyl ether of which when hydrolysed, diazotised, and boiled with alcohol gives the same methyl ether as is obtained by the action of methyl sulphate on 5-nitro-1-naphthol (Kaufler and Bräuer, Abstr., 1907, i, 799). 5-Nitro-8-acetylamino-1-naphthol changes colour at 192°, but has m. p. 240°.

4-Benzeneazo-5-nitro-8-acetylamino-1-naphthol, $C_{18}H_{14}O_4N_4$, obtained by condensing benzenediazonium chloride with an alcoholic alkaline solution of the 5-nitro-8-acetylamino-1-naphthol, forms dark red crystals with a metallic lustre and m. p. 220°.

5-Nitro-8-amino-1-naphthyl methyl ether, $C_{11}H_{10}O_3N_2$, forms large, reddish-brown crystals, m. p. 193°. 5-Nitro-1-naphthyl methyl ether, $C_{11}H_9O_3N$, forms slender, yellow needles, m. p. 96–97°.

When α -naphthyl acetate is nitrated at 0° with nitric acid (D 1.38), a 60% yield of 2:4-dinitro-1-naphthol and a 5% yield of 2-nitro-1-naphthyl acetate are obtained.

8-Tolylsulphonylamino-1-naphthol, $OH \cdot C_{10}H_7 \cdot NH \cdot SO_2 \cdot C_7H_5$, obtained by heating 8-amino-1-naphthol sulphate, *p*-toluenesulphonyl chloride, and sodium acetate with acetic acid, forms colourless prisms, m. p. 189°.

8-Acetylamino-1-naphthyl ethyl ether, $OEt \cdot C_{10}H_7 \cdot NHAc$, crystallises in broad, glistening plates, m. p. 154. J. J. S.

Compounds of Hexamethylenetetramine with Multivalent Alcohols. E. GRISHKEWITSCH-TRUCHIMOWSKY (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1324–1325).—Hexamethylenetetramine reacts with multivalent alcohols, forming crystalline, complex compounds, which are deposited in almost quantitative yield when aqueous solutions of the amine and alcohol are mixed.

Resorcinol gives the compound, $C_6H_{12}N_4 \cdot C_6H_4(OH)_2$, which forms shining, oblique prisms, begins to turn yellow at 125°, and decomposes completely at about 200°.

Catechol yields the compound, $C_6H_{12}N_4 \cdot 2C_6H_4(OH)_2$, in slender needles, decomp. about 160°.

Pyrogallol gives the compound, $2C_6H_{12}N_4 \cdot 3C_6H_3(OH)_3$, forming small needles, decomp. about 145°. T. H. F.

Tertiary Alcohols of the Tollylallyl Series. E. GRISHKEWITSCH-TRUCHIMOWSKY (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1326–1332. Compare Abstr., 1909, i, 151).—*p*-Tolylethylallylcarbinol,

$C_6H_4Me \cdot CEt(CH_2 \cdot CH \cdot CH_2) \cdot OH$, prepared by the action of magnesium on a mixture of *p*-tolyl ethyl ketone and allyl bromide, is a yellow, viscous liquid with an intense, characteristic odour, b. p. 133–135°/18 mm., D_4^{20} 0.9664, n_D^{20} 1.52093. On oxidation, it gives the corresponding acid and trihydric alcohol, to be described later.

The intermediate *organo-magnesium compound*,
 $\text{C}_6\text{H}_4\text{Me}\cdot\text{C}(\text{Et})(\text{C}_6\text{H}_5)\cdot\text{O}\cdot\text{MgBr}\cdot\text{OEt}_2$,
 formed in the above reaction, separates in almost colourless
 prisms.

p-Tolylpropylallylcarbinol, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CPr}^a(\text{C}_6\text{H}_5)\cdot\text{OH}$, prepared by
 the action of magnesium on a mixture of *p*-tolyl propyl ketone and
 allyl bromide, is a viscous, colourless liquid with an intense,
 characteristic odour, b. p. $138\text{--}139^\circ/13\text{ mm.}$, D_4^{20} 0.9531,
 n_D^{20} 1.51682.

p-Tolylisopropylallylcarbinol, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CPr}^i(\text{C}_6\text{H}_5)\cdot\text{OH}$, obtained by
 the action of magnesium on a mixture of *p*-tolyl isopropyl ketone
 and allyl bromide, is a viscous, colourless liquid of aromatic odour,
 b. p. $140\text{--}143^\circ/21\text{ mm.}$, $D_4^{19.5}$ 0.9542, $n_D^{19.5}$ 1.51385.

Comparison of the physical constants of these alcohols and those
 of *p*-tolylmethylallylcarbinol (*loc. cit.*) shows that passage from any
 one member of the series to the next higher homologue is accom-
 panied by a rise of $5\text{--}7^\circ$ in the b. p., a diminution of $0.017\text{--}0.013$
 in the value of D , an increase in the value of n , and an increase
 of about 5 in the molecular refraction (Lorenz and Lorentz's formula).
 Isomeric alcohols of this series differ but slightly in b. p., and have
 almost identical values for D and for the molecular refraction.

T. H. P.

**Action of Magnesium on a Mixture of Allyl Bromide and
 Benzophenone: Synthesis of Diphenylallylcarbinol.** B. TARASOFF
(J. Russ. Phys. Chem. Soc., 1909, 41, 1309--1313).—Diphenylallyl-
 carbinol, $\text{C}_6\text{H}_5\cdot\text{CPh}_2\cdot\text{OH}$ (compare Javorsky, Abstr., 1908, i, 753), is
 a viscous, pale yellow liquid with a characteristic odour and a bitter
 taste, b. p. $300^\circ/760\text{ mm.}$ (decomp.), $183\text{--}184^\circ/27\text{ mm.}$, D_4^{23} 1.0720,
 n_D^{23} 1.59179. It decolorises bromine readily, and on oxidation with
 1.5 times the theoretical proportion of potassium permanganate,
 yields *aa*-diphenylbutane- $\alpha\gamma\delta$ -triol,



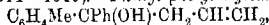
which crystallises in small, pale yellow, hygroscopic needles, m. p.
 $136\text{--}137^\circ$.

More vigorous oxidation of diphenylallylcarbinol (1 mol.) by means
 of permanganate (4 atoms of oxygen) yields β -hydroxy- $\beta\beta$ -diphenyl-
 propionic acid (compare Rupe and Busolt, Abstr., 1908, i, 23).

In one instance the action of magnesium on a mixture of allyl
 bromide and benzophenone yielded, instead of diphenylallylcarbinol,
 a product which, when distilled under diminished pressure, gave
 water and then a heavy, dark red liquid, b. p. about $290\text{--}292^\circ$, with
 a characteristic hydrocarbon odour.

T. H. P.

**Action of Magnesium on a Mixture of Phenyl *p*-Tolyl
 Ketone and Allyl Bromide.** W. KUZMIN *(J. Russ. Phys. Chem.*
Soc., 1909, 41, 1314--1319).—Phenyl-*p*-tolylallylcarbinol,



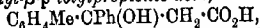
obtained by the action of magnesium on a mixture of allyl
 bromide and phenyl *p*-tolyl ketone, is a colourless liquid, b. p.
 $201\text{--}202^\circ/30\text{ mm.}$

α-Phenyl-α-p-tolylbutane-α,δ-triol,



prepared by oxidising phenyl-*p*-tolylallylcarbinol with 1% permanganate solution, forms nodular crystals, m. p. 149—150°.

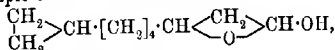
β-Hydroxy-β-phenyl-β-p-tolylpropionic acid,



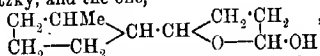
prepared by oxidising phenyl-*p*-tolylallylcarbinol by means of 4% permanganate solution, forms rosettes or nodular masses of acicular crystals, and begins to decompose at 181°. Its silver, potassium, and copper salts were prepared.

T. H. P.

Structure of Naphthenic Acids. K. W. CHARITSCHKOFF (*Jb. Russ. Phys. Chem. Soc.*, 1909, 41, 1150—1152).—The structure of the naphthenic acids isolated from natural naphtha still remains undecided, descriptions which have been given of these acids often containing no information concerning either their characteristic reactions or their derivatives. These acids exhibit distinctly acid properties, forming stable salts with many metallic oxides, and, in some cases, displacing mineral acids, for example, from copper and silver salts; whilst, on the other hand, they present the properties of anhydrides and alcohols, as they give Rosenthaler's reaction with hydrochloric acid and vanillin, and form chloro-anhydrides, which are decomposed with difficulty by water, or an alkali yielding the corresponding acids, together with compounds of unknown constitution resembling simple ethers. The formula,

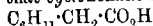


given by Zalozetzky, and the one,

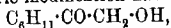


given by Brun (Wischin, *Die Naphtene*, 28), and also other formula which have been given for decanaphthenic acid, do not explain the acidic function possessed by the hydroxyl group.

The suggestion is made that cyclohexane-3-acetic acid,



(compare Zelinsky and Alexandroff, *Abstr.*, 1902, i, 74), may be capable of existing in a tautomeric modification having the formula



which would explain the alcoholic properties exhibited by the acid.

T. H. P.

Synthesis of Aromatic Amino-acids. IV. Direct Carboxylation of Dimethylaniline in the Nucleus. Rearrangement of Alkylphenylcarbonates into *p*- and *o*-Alkylaminobenzoates. JOSEF HOUBEN and ROBERT FREUND (*Ber.*, 1909, 42, 4815—4825).—The formation of dimethylaminobenzoic acid when methylaniline, alkyl iodide, magnesium and carbon dioxide are heated at 200° in presence of dimethylaniline suggests that the last substance acts as a methylating agent, and that possibly the introduction of the group CO_2MgI into the nucleus of methylaniline facilitates the

methylation of the methylamino-group. On the other hand, no methylaminobenzoate is formed on prolonged heating of magnesium aminobenzoate with dimethylaniline. Probably magnesium methyl iodide and dimethylaniline first interact, forming methane and iodomagnesiumdimethylaniline, $\text{IMg}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, and this forms an additive compound with carbon dioxide, yielding the *p*-dimethylaminobenzoate. In agreement with this hypothesis, the salt of *p*-dimethylaminobenzoic acid is formed when *p*-toluidine, dimethylaniline, and methyl magnesium iodide are heated in a stream of carbon dioxide at $190\text{--}200^\circ$. *p*-Dimethylaminobenzoic acid is formed when magnesium methyl iodide and dimethylaniline are heated in carbon dioxide at 215° in open vessels or under pressure. The formation of an inflammable gas, probably methane, was also observed.

No salt of *p*-dimethylaminobenzoic acid is formed when dimethylaniline is heated with iodomagnesium acetate or formate, with or without carbon dioxide; this disposes of the possibility that carbon dioxide and magnesium methyl iodide first react to form iodomagnesium acetate.

p-Dimethylaminobenzoic acid is the main product when carbon dioxide and methylaniline magnesium iodide are heated under considerable pressure, but at the same time small quantities of an *o*-methylamino-acid are formed, crystallising in well formed blue, glistening needles, and fluorescing blue in alcoholic solution; this is probably methylanthranilic acid.

On heating carbon dioxide and ethylaniline magnesium iodide, a mixture of *p*-diethylaminobenzoic acid, m. p. 193° , and *p*-ethylaminobenzoic acid, together with traces of methylanthranilic acid, is obtained.

When carbon dioxide is heated at 220° under 10 atmospheres pressure with magnesium ethyl iodide and a mixture of mono- and di-ethylaniline, both *p*-diethylaminobenzoic acid, m. p. 190° , and *p*-ethylaminobenzoic acid, m. p. $177\text{--}178^\circ$, are formed. *p*-Acetyl-ethylaminobenzoic acid forms colourless platelets, m. p. 180° ; the chloroacetyl derivative also crystallises in colourless, flat plates, m. p. $163\text{--}164^\circ$; the carboxy-compound separates in needles, m. p. 130° .

E. F. A.

Benzylamineacrylic Acids (ω -Aminomethylcinnamic Acids).

ALFRED EINHORN and MAXIMILIAN GÖTLER (*Ber.*, 1909, **42**, 4837—4850).—Methylolchloroacetamide and cinnamic acid interact in presence of concentrated sulphuric acid, forming a mixture of ω -chloroacetyl-amino-*p*- and -*m*-methylcinnamic acids. The two isomerides may be separated by means of acetone, in which the *para*-derivative is sparingly soluble.

Ethyl ω -chloroacetyl-amino-*p*-methylcinnamate interacts with diethylamine or piperidine, forming ethyl ω -diethyl- or piperidyl-glycylamino-*p*-methylcinnamate, which is hydrolysed by hydrobromic acid to the corresponding acid.

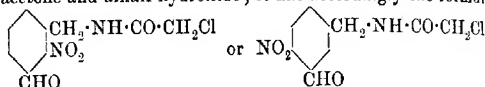
When boiled with hydrochloric acid, ω -chloroacetyl-amino-*p*-methylcinnamic acid is converted into the hydrochloride of ω -amino-*p*-methylcinnamic acid, from which the free acid is obtained on evaporation.

with ammonia. ω -Amino-*p*-methylcinnamic acid forms terephthalic acid on oxidation with permanganate; nitrous acid converts it into *p*-methylcinnamic acid.

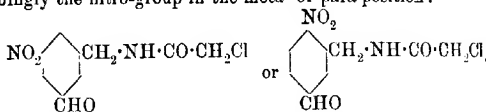
On nitration of ω -chloroacetylamino-*p*-methylcinnamic acid, a mixture of two isomeric mononitro-acids, m. p. 171–172° and 224–225°, is formed.

The less fusible acid is converted into a nitro- ω -chloroacetylamino-*p*-tolualdehyde on oxidation, which, since it is coloured blue by acetone and alkali hydroxide, contains the nitro- and COH-groups in the adjacent positions; therefore it must be *o*-nitro- ω -chloroacetylamino-*p*-methylcinnamic acid; the more fusible isomeride is *m*-nitro- ω -chloroacetylamino-*p*-methylcinnamic acid.

Two mononitro-derivatives are similarly formed from ω -chloroacetylamino-*m*-methylcinnamic acid, m. p. 220° and 198° respectively. The latter gives on oxidation nitro- ω -chloroacetylamino-*m*-tolnaldehyde, which forms a claret-red phenylhydrazone and gives a blue coloration with acetone and alkali hydroxide; it has accordingly the formula:



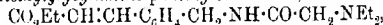
The nitro-acid, m. p. 220°, is the main product; it forms a nitro-aldehyde giving a greenish-red colour with acetone and alkali, and has accordingly the nitro-group in the meta- or para-position:



Cinnamic acid is dissolved in much concentrated sulphuric acid, and methylchloroacetamide slowly added in the cold; about 70% of the theoretical quantity of the condensation product is obtained. Permanganate oxidises it into a mixture of terephthalic and isophthalic acids, identified by their dimethyl esters. By treatment with acetone the product is separated into ω -chloroacetylamino-*p*-methylcinnamic acid, $\text{CO}_2\text{H} \cdot \text{CH} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2\text{Cl}$, crystallising in well formed needles, m. p. 210°, and ω -chloroacetylamino-*m*-methylcinnamic acid, which separates in starch-like, crystalline aggregates, m. p. 152–156°.

The ethyl ester of the former crystallises in bunches of intergrown needles, m. p. 106–107°; the methyl ester has m. p. 96–97°.

Ethyl ω -diethylglycylamino-*p*-methylcinnamate,



was obtained as an oil on condensation of the above ester with diethylamine; the salts were also oily, with the exception of the picrate, which crystallises in golden-yellow plates, m. p. 152°. The hydrobromide of the corresponding acid crystallises in fatty, glistening plates, m. p. 212°.

Ethyl cine, alkyl *lycyl*amino-*p*-methylcinnamate is a thick fluid oil; the salt in presence of picric acid crystallises in platelets, m. p. 170°. The hydrobromide acts as a methyl ester crystallises in glistening plates, m. p. 226–227°. The group CO_2MgI in cinnamic acid, $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CH} \cdot \text{CO}_2\text{H}$,

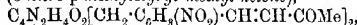
crystallises in plates, which do not melt at 320°. The *hydrochloride* forms stellar aggregates of lustrous needles, m. p. 295—296°. The acid interacts with monochloroacetic anhydride, forming the *ω*-chloroacetyl described above.

ω-Amino-*m*-methylcinnamic acid crystallises in prismatic needles, which darken at 200°, m. p. 243—244° (decomp.). The *hydrochloride* forms quadratic plates or rhomboids.

p-Methylcinnamic acid, $\text{OH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, prepared by the action* of sodium nitrite on the amino-*p*-methylcinnamic acid separates in indefinite, flocculent aggregates or needles, m. p. 200—201°.

2-Nitro-*ω*-chloroacetyl-amino-*p*-methylcinnamic acid crystallises in colourless needles, m. p. 224—225°; the *ethyl* ester forms very minute needles, m. p. 143—144°.

3-Nitro-*ω*-chloroacetyl-amino-*p*-tolualdehyde crystallises in minute rhombohedra, m. p. 171° (decomp.). When warmed with concentrated hydrochloric acid, it becomes at first violet-red, later a dirty green; and subsequently a black powder separates. The *phenylhydrazone* forms garnet-red prisms, m. p. 191—192° (decomp.). The aldehyde condenses with acetone in presence of sodium hydroxide to *diketo-piperazinobis* (*o*-nitro-*p*-methylstyryl methyl ketone),



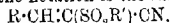
crystallising in matted needles, which darken at 230°, m. p. 242° (decomp.).

3-Nitro-*ω*-chloroacetyl-amino-*p*-methylcinnamic acid forms strongly refractive plates, m. p. 171—172°; the *ethyl* ester forms rectangular platelets, m. p. 105°.

4- or 5'-Nitro-*ω*-chloroacetyl-amino-*m*-methylcinnamic acid crystallises in needles, m. p. 220°; the *ethyl* ester separates in prisms, m. p. 148—150°.

5- or 6-Nitro-*ω*-chloroacetyl-amino-*m*-tolualdehyde forms refractive parallelogram-like plates, m. p. 198—199°, and gives an intense red coloration with acetone and alkali. *o*-Nitro-*ω*-chloroacetyl-amino-*m*-methylcinnamic acid crystallises in leaflets, m. p. 198°; the *ethyl* ester forms refractive platelets, m. p. 241—242° (decomp.). *o*-Nitro-*ω*-chloroacetyl-amino-*m*-tolualdehyde forms bunches of needles, m. p. 125°; it gives an intense blue coloration on warming with acetone and sodium hydroxide. The *phenylhydrazone* crystallises in needles aggregated in bunches, m. p. 174°. E. F. A.

Some Condensation Products from Arylsulphonated Acetonitriles and Aromatic Aldehydes. JULIUS TRÜGER and H. BREMER (*Arch. Pharm.*, 1909, 247, 613—617).—The following compounds have been obtained by the method described previously (*Abstr.*, 1908, i, 798); the notation is the same, namely,



$\text{R} = p\text{-C}_6\text{H}_4\cdot\text{NMe}_2$, $\text{R}' = \text{Ph}$, red needles with blue fluorescence, 194°; $\text{R} = p\text{-C}_6\text{H}_4\text{Pr}^t$, $\text{R}' = \text{Ph}$, pale yellow needles, 78°; $\text{R} = p\text{-C}_6\text{H}_4\cdot\text{OH}$, $\text{R}' = \text{Ph}$, yellowish-white crystals, 214°; $\text{R} = p\text{-C}_6\text{H}_4\cdot\text{NMe}_2$, $\text{R}' = \beta\text{-C}_{10}\text{H}_7$, red crystals, 197°; $\text{R} = p\text{-C}_6\text{H}_4\text{Pr}^t$, $\text{R}' = \beta\text{-C}_{10}\text{H}_7$, large prisms,

146°; $R = p\text{-C}_6\text{H}_4\cdot\text{OH}$, $R' = p\text{-C}_6\text{H}_4$, yellow crystals, 157°; $R = p\text{-C}_6\text{H}_4\cdot\text{NH}_2$, $R' = p\text{-C}_6\text{H}_4\cdot\text{Cl}$, red rhombohedra, 245—246°;
 $R = p\text{-C}_6\text{H}_4\cdot\text{OH}$, $R' = p\text{-C}_6\text{H}_4\cdot\text{Cl}$,
 yellow prisms, 154—156°; $R = p\text{-C}_6\text{H}_4\cdot\text{NMe}_3$, $R' = p\text{-C}_6\text{H}_4$, red crystals with blue fluorescence, 217°; $R = p\text{-C}_6\text{H}_4\cdot\text{OH}$, $R' = p\text{-C}_6\text{H}_4$, leaflets, 133—135°; $R = p\text{-C}_6\text{H}_4\cdot\text{NMe}_3$, $R' = p\text{-C}_6\text{H}_4\cdot\text{Br}$, red prisms with blue shimmer, 240—241°; $R = p\text{-C}_6\text{H}_4\cdot\text{OH}$, $R' = p\text{-C}_6\text{H}_4\cdot\text{Br}$, yellow prisms, 166°; $R = p\text{-C}_6\text{H}_4\cdot\text{NMe}_3$, $R' = p\text{-C}_6\text{H}_4\cdot\text{I}$, ruby-red crystals with blue shimmer, 222°; $R = p\text{-C}_6\text{H}_4\cdot\text{NMe}_3$, $R' = \text{C}_6\text{H}_5\text{Me}$, light red prisms, 192°; $R = p\text{-C}_6\text{H}_4\cdot\text{OH}$, $R' = \text{C}_6\text{H}_5\text{Me}$, yellow prisms, 181°.
 C. S.

Halogen-amino-acids. VIII. Position of the Iodine Atoms in Di-iodotyrosine (Iodogorgonic Acid). HENRY L. WHEELER and CARL O. JOHNS (*Amer. Chem. J.*, 1910, **43**, 11—19).—Wheeler and Jamieson (Abstr., 1905, i, 350) synthesised iodogorgonic acid, and showed it to be a di-iodotyrosine, probably the 3:5-compound. This configuration has now been confirmed.

Di-iodotyrosine, when treated with methyl iodide and potassium hydroxide, is converted into a compound, provisionally regarded as $\text{OMe}\cdot\text{C}_6\text{H}_3\text{I}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NMe}_3\text{I})\cdot\text{CO}_2\text{H}$. On boiling this substance with sodium hydroxide, sodium 3:5-di-iodo-*p*-methoxycinnamate is obtained, and, when acidified with hydrochloric acid, is converted into the corresponding acid, $\text{OMe}\cdot\text{C}_6\text{H}_3\text{I}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CO}_2\text{H}$, m. p. 202—203°, which forms minute prisms or long, silky needles. This acid has also been prepared by the methylation of 3:5-di-iodo-*p*-hydroxy-cinnamic acid (Paal and Mohr, Abstr., 1897, i, 53), which has m. p. 247° (decomp.). The potassium, barium, silver, mercury, and copper salts of 3:5-di-iodo-*p*-methoxycinnamic acid are described. The methyl ester, m. p. 173—174°, crystallises in thin plates, and the ethyl ester, m. p. 135°, in small, colourless prisms. E. G.

Conversion of Stable Stereoisomeric Ethylene Derivatives into the Labile Modifications by Ultraviolet Light. RICHARD STOERMER (*Ber.*, 1909, **42**, 4865—4871).—In connexion with the stereoisomerides of substituted ethylenes, the conversion of the labile into the stable modification by the action of light, particularly in the presence of a halogen, is not uncommon. The converse change, produced by light alone, has been remarked in very few cases (Paal and Schultze, Abstr., 1902, i, 228; Ciamician and Silber, *ibid.*, 1904, i, 161).

Perkin has noted the conversion of methylcoumarinic acid into methylcoumaric acid by sunlight (*Trans.*, 1881, **39**, 409), but the author finds that in the coumaric acid series the tendency is the other way, the stable form changing to the labile under the influence of ultraviolet light. Thus Perkin's change occurs only to the extent of 25%, whereas coumaric acid yields 75% of coumarin, methylcoumaric acid yields 75% of methylcoumarinic acid, ethylcoumaric acid yields ethylcoumarinic acid quantitatively, and acetylcoumaric acid is also quantitatively changed to acetylcoumarinic acid.

That the changes are caused by the ultraviolet rays is proved by

means of light filters, the interposition of a filter which absorbs ultraviolet light between the lamp and the solution preventing any change of the stable to the labile modification. Hence the less fusible stable forms of stereoisomeric compounds can be changed directly, under definite conditions, into the more reactive labile modifications if energy is supplied by ultraviolet light. Thus the stable form of *o*-anisyleinnamic acid, which could not be changed into the labile modification by Stoermer and Frederici (Abstr., 1908, i, 179), has now been converted to the extent of 50% by using a more intense light. In the case of stereoisomeric α -alkylated acids, the conversion of the stable into the labile form is a matter of great difficulty. The case of cinnamic acid is interesting. A benzene solution of ordinary cinnamic acid is exposed for eight days to the light of a Uviol lamp, with the result that 25–30% of Liebermann's isocinnamic acid, m. p. 58°, is produced. *allo*Cinnamic acid in benzene is converted into ordinary cinnamic acid under similar conditions. Also fumaric acid changes to maleic acid in eight days, but the conversion of mesaconic acid into citraconic acid is very difficult, these being α -methylated acids. When stilbene in benzene is exposed to ultraviolet light for eight days, it is converted to the extent of about 90% into isostilbene, which can be reconverted into stilbene by heating at 170–180° for one hour, by the vapour of fuming nitric acid in a few minutes, and quantitatively by exposure to sunlight of its solution in carbon disulphide containing a trace of bromine.

C. S.

General Synthesis of Phenylated Fatty Acids. FERDINAND MAUTHNER (*Annalen*, 1909, 370, 368–375. Compare Abstr., 1908, i, 986).—Derivatives of acetic acid, containing as a substituent either a phenyl or substituted phenyl group, may be prepared from the corresponding aromatic aldehydes by the following series of changes: (1) $R \cdot \text{CHO} + \text{NHBz} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} = 2\text{H}_2\text{O} + \text{NBz} \cdot \text{C} \begin{smallmatrix} \text{CO} \\ \text{C:CHR} \end{smallmatrix}$;

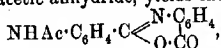
(2) $\text{NBz} \cdot \text{C} \begin{smallmatrix} \text{CO} \\ \text{C:CHR} \end{smallmatrix} \xrightarrow[\text{NaOH}]{\text{Aqueous}} \text{NH}_3 + \text{Ph} \cdot \text{CO}_2\text{H} + \text{CH}_2\text{R} \cdot \text{CO} \cdot \text{CO}_2\text{H}$, and (3)

$\text{CH}_2\text{R} \cdot \text{CO} \cdot \text{CO}_2\text{H} + \text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{CO}_2 + \text{CH}_2\text{R} \cdot \text{CO}_2\text{H}$. The isolation of the substituted pyruvic acid is unnecessary; the solution obtained by boiling the azlactone with a dilute aqueous solution of sodium hydroxide is treated with hydrogen peroxide at the ordinary temperature. In order to exemplify its general applicability, phenylacetic acid, *p*-hydroxyphenylacetic acid, *o*-methoxyphenylacetic acid, *p*-methoxyphenylacetic acid, homovanillic [4-hydroxy-3-methoxyphenylacetic] acid, and homopiperonic [methylenedioxyphenylacetic] acid have been prepared by this method.

The following azlactones are prepared by heating the necessary aldehyde with hippuric acid, acetic anhydride, and sodium acetate on a water-bath. 3-Acetoxy-4-methoxy-(α)-benzoyliminocinnamic anhydride, $\text{C}_{19}\text{H}_{15}\text{O}_5\text{N}$, has m. p. 194–195°. 2-Methoxy-(α)-benzoyliminocinnamic anhydride, $\text{C}_{17}\text{H}_{13}\text{O}_5\text{N}$, crystallises in yellow leaflets, m. p. 165–166°.

W. H. G.

Lactonoid Anhydrides of Acylated Amines. I. The Lactones of Acetylanthranoylanthranilic Acid and of Acetylanthranilic Acid. ERNST MOHR and FRIEDRICH KÖHLER (*J. pr. Chem.*, 1909, [iii], 80, 521—546).—Anthranoylanthranilic acid, when boiled with excess of acetic anhydride, yields the lactone,



and not acetylanthranoylanthranilic acid (Anschütz, Schmidt, and Greiffenberg, Abstr., 1903, i, 57). The formation of this characteristic lactone is one of the best criteria for the recognition of anthranoylanthranilic acid.

Anthranilic acid or acetylanthranilic acid, when heated with acetic anhydride, yields acetylanthranil, $\text{CMe:N} \begin{array}{l} \nearrow \text{O} \cdot \text{CO} \\ \searrow \end{array} \text{C}_6\text{H}_4$ (Bredt and Hof,

Abstr., 1900, i, 229; Anschütz and Schmidt, *ibid.*, 1903, i, 56), and benzoylanthranilic acid yields a similar lactone (Angeli and Angelica, Abstr., 1901, i, 46; Heller and Fiesselmann, *ibid.*, 1902, i, 780). Thionyl chloride transforms anthranoylanthranilic acid into a lactone, m. p. 162° (Schroeter, Abstr., 1907, i, 530), which reacts with acetic anhydride, yielding acetylanthranoylanthranilic acid lactone.

Benzoylated α -amino-fatty acids are also capable of losing water in a similar manner, yielding lactones (Erlenmeyer, Abstr., 1893, i, 580; 1899, i, 759; 1900, i, 549; compare also Mohr and Geis, Abstr., 1908, i, 339, and Mohr and Stroschein, *ibid.*, 1909, i, 581).

These lactones are intermediate in properties between acid anhydrides and lactones, and belong to Hans Meyer's second class of lactones (Abstr., 1900, i, 9). They combine readily with ammonia, yielding amides of the type $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH}_2$, which lose the elements of water when boiled with sodium hydroxide solution, yielding cyclic imides, for example, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{array}{l} \nearrow \text{N} \cdot \text{C}_6\text{H}_4 \\ \searrow \text{NH} \cdot \text{CO} \end{array}$.

The possibility of a lactam structure, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{N} \begin{array}{l} \nearrow \text{C}_6\text{H}_4 \\ \searrow \text{CO} \end{array}$, for the lactone of acetylanthranoylanthranilic acid is discussed, but rejected (compare Bamberger, Abstr., 1903, i, 432; 1909, i, 509).

Acetylanthranoylanthranilic acid crystallises in colourless needles, m. p. 221.5—223° (Anschütz, Schmidt, and Greiffenberg, 225—226°). The sodium salt crystallises in thin, flexible needles. The lactone,

$\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{array}{l} \nearrow \text{N} \cdot \text{C}_6\text{H}_4 \\ \searrow \text{O} \cdot \text{CO} \end{array}$, crystallises in pale yellow plates or needles,

m. p. 211—212°. When warmed with sodium hydroxide solution, it yields ultimately acetic and anthranilic acids. When boiled with alcoholic ammonia, the lactone yields acetylanthranoylanthranilamide, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH}_2$, which crystallises in glistening, snow-white prisms, m. p. 226—227° (decomp.). The imide, 2-*o*-aminophenyl-3 : 4-dihydro-1 : 3-quinazalone, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{array}{l} \nearrow \text{N} \cdot \text{C}_6\text{H}_4 \\ \searrow \text{NH} \cdot \text{CO} \end{array}$,

obtained by boiling the above amide with 6*N*-sodium hydroxide solution and precipitating with acetic acid, crystallises in lemon-

yellow needles, m. p. 237°, and has both feebly basic and acidic properties. The sodium salt and the hydrochloride have been prepared.

The acetyl derivative, $C_{18}H_{19}O_2N_3$, crystallises in very pale yellow prisms, m. p. 278° (decomp.), and yields a sparingly soluble sodium derivative.

The name lactimones (Abstr., 1908, i, 339; 1909, i, 581) for this type of lactone is withdrawn.
J. J. S.

Lactonoid Anhydrides of Acylated Amino-acids. II. Lactone of α -Benzoylaminoisobutyric Acid. ERNST MOHR [with THEODOR GEIS] (*J. pr. Chem.*, 1910, [ii], 81, 49—73. Compare Abstr., 1908, i, 339).—A more detailed account of work already published. The lactimone, $CM_2 \begin{smallmatrix} N=CPh \\ \diagup \quad \diagdown \\ CO \quad O \end{smallmatrix}$ (*loc. cit.*), is a very reactive substance, yielding α -benzoylaminoisobutyranilide,

$NHBz \cdot CM_2 \cdot CO \cdot NHPh$,
m. p. 228—229°, with aniline; the chloride, $NHBz \cdot CM_2 \cdot COCl$, m. p. 148—150° (decomp.), with dry hydrogen chloride, and α -benzoylaminoisobutyrylglycine, $NHBz \cdot CM_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$, m. p. 191°, by heating with glycine at 140—170°.

Ethyl α -benzoylaminoisobutyrate has m. p. 123°, and the methyl ester, m. p. 124°.
C. S.

Condensation of *p*-Hydroxybenzoic Acid with Formaldehyde. FELIX EPSTEIN (*J. pr. Chem.*, 1910, [ii], 81, 85—93).—The interaction of *p*-hydroxybenzoic acid, 40% formaldehyde, and dilute hydrochloric acid for eight to ten hours on the water-bath results in the formation of 2:2'-dihydroxydiphenylmethane-5:5'-dicarboxylic acid, $[CO_2H \cdot C_6H_3(OH)]_2CH_2$, an ill-defined substance which carbonises by heating and does not yield crystalline derivatives; the copper salt, $C_{15}H_{10}O_8Cu \cdot 3H_2O$, and the diacetyl derivative, $C_{19}H_{16}O_8$, have been prepared. By prolonged heating with concentrated sulphuric acid, it is converted into a green sulphoxanthinedicarboxylic acid, $C_{15}H_{10}O_8S$, which forms a green copper salt, $(C_{15}H_7O_8S)_2Cu_2$.
C. S.

New Method of Preparing Ellagic Acid. L. V. BUSCHUEFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1484—1488).—The action of Berthollet's salt and hydrochloric acid on protocatechuic acid yields katellagic acid, whilst gallic acid under the same treatment gives ellagic acid.
T. H. P.

Preparation of Acids and Amides from Phenyl Alkyl Ketones by means of Yellow Ammonium Sulphide. CONRAD WILLGERODT and WILHELM HAMBRECHT (*J. pr. Chem.*, 1910, [ii], 81, 74—85).—The behaviour of *p*-tolyl alkyl ketones is exactly analogous to that of phenyl alkyl ketones in the reaction described previously (Abstr., 1909, i, 716) provided the conditions therein mentioned are strictly adhered to. The yields of amide and acid are less the greater the carbon content of the alkyl groups, and the preparation of fatty
VOL. XXVIII, i. L

aromatic acids by means of Willgerodt's reaction reaches its limit between the valeryl and the heptyl ketones.

p-Tolyl methyl ketone and yellow ammonium sulphide at 220° give 45% of *p*-tolylacetamide and 8–10% of *p*-tolylacetic acid, whilst with colourless ammonium sulphide, 2:5-di-*p*-tolylthiophen and 2:4-di-*p*-tolylthiophen are obtained in addition to the preceding amide and acid. Similarly, *p*-tolyl ethyl ketone and yellow ammonium sulphide at 210° yield 30% of *p*-tolylpropionamide and 6–8% of the corresponding acid. *p*-Tolyl propyl ketone, $C_6H_4 \cdot COPr^a$, b. p. 247–248°, prepared from butyryl chloride and toluene in carbon disulphide in the presence of aluminium chloride, forms a *phenylthiohydrazone*, m. p. 73°, and by the Willgerodt reaction at 210° yields 18–20% of *p*-tolylbutyramide, m. p. 135°, and 5% of *p*-tolylbutyric acid, m. p. 60°, of which the barium and silver salts are described. *p*-Tolyl isopropyl ketone and yellow ammonium sulphide at 200° yield *p*-tolylisobutyramide, m. p. 130°, and a very small amount of *p*-tolylisobutyric acid, m. p. 85°. *p*-Tolyl isobutyl ketone, $C_6H_4 \cdot CO \cdot CH_2 \cdot CHMe_2$, b. p. 254–255°, obtained from toluene and isovaleryl chloride, forms an *oxime*, m. p. 65°, and yields 3–4% of *p*-tolylisovaleramide, m. p. 150°, and a very slight trace of the acid, m. p. 128°, in the Willgerodt reaction at 190°. *p*-Tolyl butyl ketone, m. p. 17°, b. p. 261°, and yellow ammonium sulphide at 180° yield 2% of *p*-tolylvaleramide, m. p. 113°, and an unappreciable quantity of the corresponding acid. C. S.

Preparation of Benzophenoneimine Derivatives. G. KEDDELIEN (*Ber.*, 1909, 42, 4759–4762).—A good yield of benzophenonephenylimine (diphenylmethyleneaniline; Pauly, this *Journ.*, 1877, ii, 614; Graebe, *Abstr.*, 1899, i, 702; Nägeli, *ibid.*, i, 910) can be prepared by condensing aniline and benzophenone with anhydrous zinc chloride at 160–180° for half an hour. Substituted anilines can react in a similar manner, and the stability of the product increases with the presence of negative substituents.

Diphenylmethylene-p-toluidine, $CPh_2 \cdot N \cdot C_6H_4Me$, is a viscid oil, and has b. p. 228°/15 mm., 245°/30 mm., or 360°/atm. pres.

The isomeric *meta*-derivative crystallises in rectangular, pointed prisms, m. p. 82·5°.

Diphenylmethylene-3:4-xylidine, $CPh_2 \cdot N \cdot C_6H_3Me_2$, forms rhombic plates, m. p. 122°.

Diphenylmethylene-m-nitroaniline, $CPh_2 \cdot N \cdot C_6H_4 \cdot NO_2$, crystallises in yellow cubes or hexagonal plates, m. p. 123·5°. *Diphenylmethylene-p-aminophenol*, $CPh_2 \cdot N \cdot C_6H_4 \cdot OH$, $C_2H_5 \cdot OH$, forms yellow plates, m. p. 172°, and loses its alcohol of crystallisation at 110°. It is stable towards hydrolysing agents.

Diphenylmethylenedimethyl-p-phenylenediamine, $CPh_2 \cdot N \cdot C_6H_4 \cdot NMe_2$, forms compact, orange-yellow crystals, and melts at 85° to a turbid, brown liquid, which clarifies at 93°.

A by-product, obtained in the preparation of the aniline derivative, is the zinc compound, $2NH_2Ph \cdot ZnCl_2 \cdot 2H_2O$ (Lachowicz and Bandrowski, *Abstr.*, 1888, 1281). J. J. S.

Dibenzylideneacetone [Distyryl Ketone] and Triphenylmethane. V. Nature of the Linking of the Halogen Atoms in the Ketohalides of Unsaturated Ketones. I. FRITZ STRAUS [and, in part, A. ACKERMANN and GEORG LUTZ] (*Annalen*, 1909, 370, 315—367. Compare Straus and Ecker, Abstr., 1906, i, 859; Straus and Caspari, Abstr., 1907, i, 609; Straus and Ackermann, Abstr., 1909, i, 489; Straus and Hüsey, Abstr., 1909, i, 490).—The present communication deals mainly with the difference in the reactivity of the halogens in distyrylchlorobromomethane and *p*-chlorophenyl-*p*-chlorostyrylchlorobromomethane. These substances, prepared by the action of acetyl bromide or hydrogen bromide and calcium bromide on the corresponding chloro-carbinols dissolved in benzene, are distinctly yellow, a further example of the analogy between these ketohalides and triphenylmethyl halides.

The chlorobromides are strictly analogous with the corresponding keto-chlorides in their chemical properties; for example, the power of one of the ethylene linkings to add on halogen is completely lost; the benzylideneacetophenone derivative does not combine with bromine, and distyrylchlorobromomethane combines only with 1 mol. of bromine; further, the group $>CClBr$ reacts in all cases so that only one atomic proportion of the halogen takes part in the change; thus, one mol. of the chlorobromide when acted on by water or methyl alcohol yields one mol. of hydrogen halide, about 96% of which is hydrogen bromide, the remainder being hydrogen chloride; similarly, an equivalent of halogen is eliminated from *p*-chlorophenyl-*p*-chlorostyrylchlorobromomethane when treated with an excess of silver oxide; the product is a mixture of the corresponding chlorocarbonol (about 98%) and bromocarbonol.

The rate at which the halogen in triphenylbromomethane, distyrylchlorobromomethane, diphenyldibromomethane, *p*-chlorophenyl-*p*-chlorostyrylchlorobromomethane, and the corresponding chloro-compounds is replaced by hydroxyl (compare Straus and Hüsey, *loc. cit.*) has been investigated; it is found that the reaction velocity decreases in the order given, and that the bromo-compounds are decomposed far more rapidly than the corresponding chloro-compounds.

The chlorobromides dissolve in concentrated sulphuric acid with the elimination of hydrogen halide; the reddish-violet solutions probably contain complex salts of the two sulphates, $RR_1CCl \cdot SO_4H$ and $RR_1CBr \cdot SO_4H$, with sulphuric acid; in support of this assumption it is found that the absorption spectra of the solutions differ slightly from those of the corresponding keto-chlorides. The solutions of the chlorobromides in liquid sulphur dioxide are more intensely coloured than those of the keto-chlorides, indicating a greater degree of ionisation, which probably takes place in two directions, $RR_1CCl \mid Br$ and $RR_1CBr \mid Cl$, but mainly in the manner indicated by the first formula.

Triphenylchloromethane when acted on by a *N*/₄-solution of hydrogen bromide in benzene is converted into the corresponding bromo-compound to the extent of about 85%; the reaction is a reversible one, a state of equilibrium being reached in about five minutes. Similarly, the chlorine is largely replaced by bromine when

a solution of the chloro-compound in benzene is shaken with calcium bromide; this reaction is likewise reversible. The interaction of keto-chlorides with hydrogen bromide and with calcium bromide is of a more complex character; a solution of distyryldichloromethane in benzene containing hydrogen bromide is found to contain part of this substance in equilibrium with the corresponding chloro-bromide and di-bromide, as represented by the equation: $(\text{CHPh}:\text{CH})_2\text{CCl}_2 + 2\text{HBr} \rightleftharpoons (\text{CHPh}:\text{CH})_2\text{CClBr} + \text{HBr} + \text{HCl} \rightleftharpoons (\text{CHPh}:\text{CH})_2\text{CBr}_2 + 2\text{HCl}$. Calcium bromide is found to react in a similar manner. On the other hand, when a solution of distyrylchlorobromomethane in benzene is treated with a slight excess of silver chloride, it is converted completely into the corresponding keto-chloride; this is in complete accord with the behaviour of triphenylbromomethane towards silver chloride.

The investigation has been extended to a study of the behaviour of tertiary butyl chloride and the corresponding bromide towards water, hydrogen halides, and calcium halides. It is found that these compounds are decomposed rapidly by water, and undergo reversible double decomposition when treated with a dissimilar hydrogen halide; the bromide interacts to a small extent with calcium chloride, but the chloride is not attacked by calcium bromide.

The different reactivity of the halogen atoms in the keto-chlorides and chloro-bromides is regarded by the author as due to a different form of union between the carbon atom and the two halogen atoms, the replaceable halogen being joined to the carbon by an ionogenic valency ("ionogene Valenz"); accordingly, the bromo-chlorides and keto-chlorides are to be regarded as solid solutions of two valency isomerides in a state of equilibrium; this may be represented in the case of distyrylchlorobromomethane thus: $(\text{CHPh}:\text{CH})_2\text{CCl}\cdots\text{Br} \rightleftharpoons (\text{CHPh}:\text{CH})_2\text{CBr}\cdots\text{Cl}$.

The bearing of the results obtained in this investigation on the question of the constitution of the triphenylhalogenmethanes is discussed, and the views of Baeyer (Abstr., 1909, i, 641) and Gomberg (Abstr., 1907, i, 504; 1909, i, 144) adversely criticised.

p-Chlorophenyl-*p*-chlorostyrylchlorobromomethane, $\text{C}_{15}\text{H}_{10}\text{Cl}_3\text{Br}$, crystallises in compact, pale yellow prisms, *m. p.* 98.5—99.5°; dilute solutions in liquid sulphur dioxide are violet-red, more concentrated solutions are pale yellow; a solution of the substance with stannic chloride in nitrobenzene is bluish-red.

Distyrylchlorobromomethane, $\text{C}_{17}\text{H}_{14}\text{ClBr}$, crystallises in stellate groups of large, slender, glistening, yellow leaflets, *m. p.* 91—92°; the dibromide, $\text{C}_{17}\text{H}_{14}\text{ClBr}_2$, crystallises in radially-grouped, colourless prisms and decomposes at 165—166°; the mercuribromide, $\text{C}_{17}\text{H}_{14}\text{ClBr}_2\text{HgBr}_2$, is a crystalline, green powder. W. H. G.

The Pyrogenetic Decomposition of (1) β -Benzopinacol and (2) α -Benzopinacol. MAURICE DELACRE (*Bull. Soc. chim.*, 1909, [iv], 5, 1144—1149, 1149—1153).—Both products were first carefully purified and then heated in retorts, the products of distillation being collected and separated by fractional distillation, and finally by crystallisation from appropriate solvents, where necessary. Full details of these separations are given in the original papers.

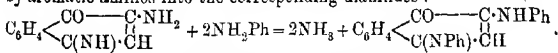
β -Benzopinacolin yielded triphenylmethane, *p*-benzoyltriphenylmethane, tetraphenylethylene, "needles," benzene, benzaldehyde, benzophenone, and unidentified products boiling at 240—320°, 340—430°, and 405—440°, and some carbonaceous residue.

α -Benzopinacolin furnished substantially the same products, with the addition of "yellow needles" and unidentified products of somewhat different boiling points. The relative yields of the various substances were not the same in the two cases. An unidentified substance, showing violet fluorescence, was present in both sets of distillation products. The "needles" were isolated from the fractions boiling at 325—380° and 380—405; this material had m. p. 144°, and may be identical with Hemilian's hydrocarbon, $C_{19}H_{14}$. The "yellow needles" obtained from α -benzopinacolin came from the same fractions as the "needles"; this product had m. p. 245°, and contained carbon, 78.8%, and hydrogen, 4.5%. T. A. H.

Action of Acetic Anhydride on Octabromo-1'-hydroxy-1-methoxy-*o*-quinol-1-monoxide. C. LORING JACKSON and H. A. FLINT (*Amer. Chem. J.*, 1910, 43, 7—11).—Jackson and Porter (Abstr., 1904, i, 254) and Jackson and Carlton (Abstr., 1905, i, 907) have shown that tetrabromo-*o*-quinone readily unites with methyl alcohol to form a compound, termed the methyl α -compound, which, when boiled with methyl alcohol, is converted into an isomeric or β -compound. Jackson and MacLaurin (Abstr., 1907, i, 223) have found that the α -compound is octabromo-1'-hydroxy-1-methoxy-*o*-quinol-1-monoxide, and that the β -compound is octabromo-1'-hydroxy-1-methoxy-*o*-quinol-1:2:2-trioxide. These authors also found that by the action of acetic anhydride on the α -compound, two substances were produced, one of which was yellow and had m. p. 225°, whilst the other was white and had m. p. 218°.

A further study of the yellow compound has shown that, when pure, it has m. p. 244° (decomp.), and that it is identical with heptabromo-*o*-quinocatechol hemi-ether (Jackson and Russe, Abstr., 1906, i, 288). On treating this substance with hot acetic anhydride, it is converted into hexabromo-*o*-quinocatechol ether (Jackson and Koch, Abstr., 1901, i, 597). When heptabromo-*o*-quinocatechol hemi-ether is shaken with 10% solution of sodium hydroxide, a substance, m. p. about 240° (decomp.), is obtained, which forms white, rhombic crystals. E. G.

Aminoanilide and Certain New Dianilides of α -Naphthaquinone. OSWALD MILLER and J. SMIRNOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1420—1421).—In acetic acid solution, amino-imino- α -naphthaquinone (di-iminonaphthol) hydrochloride is converted by aromatic amines into the corresponding dianilides:



The reaction probably takes place in two stages, the first of these resulting in the formation of an aminoanilide of α -naphthaquinone, $C_6H_5 \begin{array}{c} \diagup \text{CO} \text{---} C \text{---} NH_2 \\ \diagdown \text{C(NR)} \cdot CH \end{array}$. The authors find that these intermediate aminoanilides, which have not been described previously, are obtained

when the reaction between the aromatic amine and the di-imino-naphthol hydrochloride takes place in alcoholic solution, in which the velocity of formation of dianilide from aminoanilide is less than that of the aminoanilide itself.

The aminoanilides of α -naphthaquinone are coloured, crystalline compounds, readily soluble in alcohol or dilute acid; in most cases they exhibit softening before melting. The following compounds of this type have been obtained in the pure state.

Aminoanilide, brown prisms or red needles, m. p. 121°. *Amino- α -toluidide*, red needles, m. p. 115°. *Amino-m-toluidide*, red needles, m. p. 110°. *Amino-p-toluidide*, red needles, m. p. 122.5°. *Amino-xylylide* (Me:Me:NH₂ = 1:2:4), red prisms or needles, m. p. 144°. *Amino-xylylide* (Me:Me:NH₂ = 1:3:4), pale red prisms or needles, m. p. 160°. *Amino-xylylide* (Me:Me:NH₂ = 1:4:5), reddish-brown needles, m. p. 153°. *Amino- ψ -cumitide*, red needles, m. p. 155°.

The following new dianilides of α -naphthaquinone have also been prepared. *Di- α -toluidide*, orange prisms or needles, m. p. 123.5°. *Di-m-toluidide*, red needles, m. p. 147°. *Dixylylide* (1:2:4), reddish-brown prisms or needles, m. p. 184°. *Dixylylide* (1:3:4), reddish-brown prisms, m. p. 154° (t). *Dixylylide* (1:4:5), reddish-brown prisms or needles, m. p. 114° (t).

T. H. P.

Action of Piperidine on d -Pinene Chloro-oxime. I. V. BUSCHUEFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1481—1484).—The action of piperidine on the chloro-oxime of d -pinene isolated from Russian turpentine yields (1) nitrosopinene, agreeing in all its properties with that obtained by Golubeff (Abstr., 1908, i, 902) from the l -pinene of the ethereal oil of the Siberian fir; (2) pinene nitropiperidine (compare Wallach, Abstr., 1888, 1098).

T. H. P.

Conversion of Pulegone into Menthenes. KARL AUWERS (*Ber.*, 1909, 42, 4895—4907).—3-Chloroisoterpinolene (from pulegone), when reduced with sodium and amyl alcohol, yields, not the expected isoterpinolene, but a mixture of Δ^3 and $\Delta^{4,8}$ -menthene. Hence this reduction forms an exception to the general rule regarding the addition of hydrogen to conjugated double linkings.

R. V. S.

Matico Leaves and Matico Oils. HERMANN THOMS (*Arch. Pharm.*, 1909, 247, 591—612).—Commercial matico oils rarely have the same or a similar composition, because they are prepared from various kinds of *Piper*, the constituents of which vary considerably. The author has prepared and examined matico oils from botanically individual leaf-material. Japan camphor and borneol, hitherto undetected in matico oils, have been discovered in the oil from *Piper camphoriferum*. On the contrary, cineol, parsley apiol, asarone, and matico camphor, which have frequently been found in commercial oils, could not be detected by the author in his oils. Dillapiol is present in particularly large amount in the oil from the leaves of *Piper acutifolium* var. *subverticillatum*.

C. S.

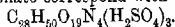
The Essential Oil of Hyacinths. C. J. ENKLAAR (*Chem. Weekblad*, 1910, 7, 1—11).—When distilled at 10 mm. pressure, the

essential oil of hyacinths yields three fractions, distilling respectively below 90° , at $92-94^{\circ}$, and between 94° and 150° . The first fraction contains a very volatile substance of disagreeable odour. When evaporated over concentrated sulphuric acid, it develops a red colour. The second fraction contains an unknown substance of powerful odour, its formula being probably $C_{15}H_{20}O$. It has b. p. $205-206^{\circ}/760$ mm., D^{20}_D 0.907, n^{20}_D 1.4914, and forms 50% of the oil. The third fraction contains benzyl benzoate and other esters (20% of the oil), an unknown fluorescent substance which is free from nitrogen (5%), and benzyl alcohol with other primary alcohols (1%). A. J. W.

Decomposition of Amygdalin. KARL FEIST (*Arch. Pharm.*, 1909, 247, 542-545. Compare Abstr., 1909, i, 589).—The synthetic production of *d*-benzaldehydecyanohydrin by the action of emulsin on benzaldehyde and hydrogen cyanide is a more rapid process, according to Auld (*Trans.*, 1909, 95, 927), than its formation by the decomposition of amygdalin by emulsin, thus indicating that its formation in the latter reaction is due to a secondary and not to a primary reaction. Since these results are exactly the reverse of those obtained previously by the author, he has repeated his experiments without adding dextrose, and confirms Auld's results. The emulsin used was obtained from Kahlbaum, that in the former experiments from Schuchardt. Since Rosenthaler (*Abstr.*, 1908, i, 817) has shown that emulsin contains a hydrolysing and also a synthesising enzyme, the discrepancy between the author's two series of experiments is attributed to the fact that Kahlbaum's emulsin contains a preponderance of the synthesising enzyme, and Schuchardt's of the hydrolysing enzyme.

The author still maintains, however, that *d*-benzaldehydecyanohydrin is a primary product of the decomposition of amygdalin by emulsin, because emulsin, freed from the synthesising enzyme by Rosenthaler's method (*Abstr.*, 1909, i, 622), acting on amygdalin and also on a mixture of benzaldehyde and hydrogen cyanide, produces in the former case a slightly dextrorotatory solution, whilst in the latter the solution remains inactive. Moreover, Walker and Kriebel have shown that the decomposition of amygdalin by sulphuric acid yields dextrose and benzaldehydecyanohydrin (*Trans.*, 1909, 95, 1369), and the author finds that when amygdalin is treated with 2.77*N*-sulphuric acid for three hours at 98° and extracted with benzene, the solution, although dark coloured, is distinctly dextrorotatory. C. S.

Crystalline Chitosan Sulphate. EMIL LÖWY (*Biochem. Zeitsch.*, 1909, 23, 47-60).—The chitosan was prepared from the shells of *Nephrops norvegicus*, from the chitin of which the chitosan was obtained by heating at $170-180^{\circ}$ with potassium hydroxide. The hydrochloride, hydrobromide, and sulphate were prepared by allowing hot solutions of the chitosan in the respective acids to cool. The concentration of the acids must be fairly high, as the chitosan is readily soluble in dilute acids. The salts were obtained crystalline. The analyses of the sulphate correspond with the formula



It can form additive products with bromine and iodine, taking up the

halogen in the proportion of one chlorine or bromine atom to two of nitrogen. It yields on hydrolysis (the products of which were quantitatively estimated) glucosamine and acetic acid, and it is assumed that the chitosan is a polymeric form of monoacetyldiglucoamine, and that the hydrolysis can be represented by the equation:

$$(C_{28}H_{50}O_{19}N_4)_x + 5xH_2O = 4x(C_6H_{13}O_5N) + 2x(CH_3 \cdot CO_2H).$$

S. E. S.

Formation of Phlobaphens. MAXIMILIAN NIERENSTEIN and T. A. WEBSTER (*Collegium*, 1909, 337—341).—Mangrove tannin is oxidised by oxygen, hydrogen peroxide, or potassium persulphate solution, yielding phlobaphens. The phlobaphen formed when oxygen is used, gave anthracene when distilled with zinc dust (compare Abstr., 1908, i, 40). The hydrogen peroxide oxidation product gave diphenylmethane when distilled with zinc, and the phlobaphen obtained by oxidising the tannin with an acetic acid solution of potassium persulphate in the presence of sulphuric acid, gave anthracene when distilled with zinc dust. The latter compound is termed *β-phlobaphen*, and the product which yields diphenylmethane, *α-phlobaphen*. The *α*-compound when boiled with dilute sulphuric acid yields the *β*-derivative. It is probable that this conversion is accompanied by the elimination of water and the formation of an anthraquinone skeleton.

J. J. S.

Constituents of the Rhizome of Imperatoria. JOHANNES HERZOG and D. KROHN (*Arch. Pharm.*, 1909, 247, 553—591).—The paper deals with a comparative examination of the crystalline constituents of the rhizomes of *Imperatoria* and *Peucedanum*. Earlier workers have shown that the latter contains peucedanin and oxypeucedanin (Schmidt, Abstr., 1899, i, 377), whilst the former contains ostruthin, oxypeucedanin, but not peucedanin (Gorup-Besanez, Abstr., 1874, 907; 1877, 717; Jassoy, Abstr., 1890, 1154). Oxypeucedanin has only once been found in the rhizome of *Imperatoria* (Heut, Abstr., 1875, 772), and then in such small amount that its identity with the oxypeucedanin of *Peucedanum* has not been certainly established.

Using their former method (Abstr., 1908, ii, 978), the authors extract the rhizomes of *Imperatoria* with boiling benzene, concentrate the extract, and treat it with light petroleum, whereby a viscous mass is separated which soon becomes crystalline. The mass is treated with ether, and the oxypeucedanin thus obtained is recrystallised successively from acetone, alcohol, and chloroform, and then has m. p. 142—143.5°; the mother liquor after fourteen days has deposited a new substance, *ostruthol*, m. p. 134—134.5°, which depresses the m. p. of oxypeucedanin and does not form an additive compound with hydrogen chloride. The benzene-light petroleum solution contains another new substance, *osthol*, m. p. 83—84°, and ostruthin. The last-mentioned substance is better isolated from the rhizome by the alcohol method recommended by Gorup-Besanez and Jassoy.

The percentage yields of these substances are: oxypeucedanin, 1.3; ostruthol, 0.3; osthol, 0.1; ostruthin, 0.5. Young two-year old rhizomes of *Peucedanum*, extracted by the benzene process, yield 2%

of peucedanin and 0.3% of oxypeucedanin, whilst old roots yield 2.5 and 0.5% respectively of the two substances. These figures refute the current view of the formation of the oxypeucedanin, for since the percentage of both peucedanin and oxypeucedanin in old rhizomes is greater than in young roots, the latter cannot be produced by oxidation at the expense of the former. The oxypeucedanin from *Imperatoria* is shown to be identical with that from *Peucedanum* by a mixed m. p. determination and by a comparison of the hydrogen chloride additive compounds.

Being able to obtain oxypeucedanin in comparatively large quantities, the authors have examined its properties more fully than previous investigators. It is optically inactive, and has m. p. 142—142.5°. The analytical data point to the formula $C_{13}H_{12}O_4$, which is confirmed by a determination of the molecular weight in glacial acetic acid and in benzene by the ebullioscopic method. By passing hydrogen chloride into a concentrated alcoholic solution at 0° and then slowly adding a large amount of water, a white, crystalline substance, m. p. 155.5—157°, is obtained, the analysis of which points to the formula $C_{26}H_{24}O_{11}Cl_2$, but the authors regard the substance as an additive compound of $C_{13}H_{12}O_4$, the discrepancy being attributed to the ready loss of hydrogen chloride. Boiling 10% sulphuric acid changes oxypeucedanin into an isomeric substance, $C_{13}H_{12}O_4$, m. p. 144—145.5°, which does not form an additive compound with hydrogen chloride. By treating oxypeucedanin with boiling 1% oxalic acid, a hydrated product, $C_{13}H_{14}O_5$, m. p. 132—133°, is obtained, which forms yellow crystals, and has a molecular weight in boiling glacial acetic acid corresponding with its formula. It readily loses water by treatment with 38% hydrochloric acid, yielding the isomeride of oxypeucedanin, m. p. 144—145.5°, which is also produced by the action of zinc and boiling acetic acid on the hydrogen chloride additive compound of oxypeucedanin. The hydrated product forms a yellow acetyl derivative, $C_{15}H_{16}O_6$, m. p. 155.5—156.5°, and a phenylurethane, $C_{26}H_{19}O_6N$, m. p. 170—170.5°, from both of which the hydrated product can be regenerated by the action of alcoholic potassium hydroxide and alcoholic ammonia respectively. Oxypeucedanin in acetone is reduced by aluminium amalgam, yielding a mixture which is separable by alcohol; the less soluble constituent, m. p. 203—205°, has a molecular weight in boiling acetic acid corresponding with the formula $(C_{13}H_{12}O_4)_2$, a result suggesting that oxypeucedanin is an unsaturated lactone. This conception is supported by the behaviour of oxypeucedanin with alkali hydroxides; with excess of alkali, it gives in aqueous-alcoholic solution yellow salts, which decompose at the ordinary temperature in neutral or faintly alkaline solution.

The authors confirm Jassoy's formula, $C_{13}H_{20}O_3$, for ostruthin by analysis, by titration with acid and alkali, and by a Zeisel estimation of the ester, $C_{18}H_{18}O_3 \cdot CO_2Me$, m. p. 64—65°, obtained by the interaction of methyl chloroformate and a strongly cooled solution of an alkali salt of ostruthin.

Osthol, $C_{15}H_{16}O_3$, m. p. 83—84°, forms long, white crystals, and contains one methoxy-group. In alcoholic solution, it yields with

hydrogen chloride an additive compound, $C_{15}H_{16}O_6 \cdot HCl$, m. p. 99.5—100°. In aqueous alcohol, it behaves with alkali hydroxides very much like oxypeucedanin, its salts in neutral or faintly alkaline solution decomposing into free alkali and osthol, which, therefore, is probably a lactone.

Osthruthol crystallises in white needles, m. p. 134—134.5°, and from the analytical data and the determination of its molecular weight in boiling benzene or methyl alcohol, has the composition $(C_8H_8O)_8$. Its behaviour with alkali hydroxides is similar to that of oxypeucedanin and osthol, the yellow solutions of the salts being decomposed by carbon dioxide. *Osthruthol* is probably a lactone. C. S.

Rhein. OTTO A. OESTERLE and G. RIAT (*Arch. Pharm.*, 1909, 247, 527—534).—Rhein, the formula of which now appears to be established beyond doubt as $C_{15}H_8O_6$, yields a dark red, crystalline potassium derivative, $C_{15}H_8O_6K_{2.9}H_2O$, and a propionate, $C_{15}H_8O_4(O \cdot CO \cdot CH_2 \cdot CH_3)_2$,

m. p. 223—224°.

Farbwerke vorm. Meister, Lucius und Brüning (D.R.-P. 158277) have shown that ethyl chloroacetate reacts easily with anthraquinone derivatives containing hydroxyl groups in the β -position, yielding ethers of ethyl glycollate. When the potassium derivative of rhein is boiled from seventeen to eighteen hours with ethyl chloroacetate, a golden-yellow, crystalline substance, $C_{23}H_{20}O_{10}$, m. p. 153—154°, is obtained, containing two ethyl glycollate residues. Since, however, the substance yields an acetyl derivative, m. p. 179—180°, in the usual way, the ethyl glycollate groups cannot have entered both the phenolic hydroxyl groups in rhein: one must be present in a hydroxyl group in a side-chain. The authors were proving that this hydroxyl group is present as a carboxyl group when Robinson and Simonsen's paper appeared (*Trans.*, 1909, 95, 1085), in which rhein is shown to be a dihydroxy-anthraquinonecarboxylic acid. The behaviour of rhein with ethyl chloroacetate is in accordance with the probability that rhein is a derivative of chrysazin (*Abstr.*, 1909, i, 946). C. S.

Chlorophyll. VIII. Degradation of Chlorophyll by Alkalis. RICHARD WILLSTÄTTER and HERMANN FRITZSCHE (*Annalen*, 1910, 371, 33—124. Compare this vol., ii, 150).—The present investigation on the products formed successively by the action of alkalis on chlorophyll is mainly an amplification of the work of Willstätter and Pfannenstiel on rhodophyllin (compare *Abstr.*, 1908, i, 198). The chlorophylls are derivatives of a tricarboxylic acid; crystalline chlorophyll contains two carbomethoxy-groups, whilst the amorphous compound contains only one carbomethoxy-group and one phytol residue. Crystalline chlorophyll, when hydrolysed, yields a tricarboxylic acid (chlorophyllin), which is acted on by methyl sulphate, yielding the corresponding trimethyl ester, a substance far more soluble than chlorophyll and very similar in composition and properties to the compound formed by the prolonged action of methyl alcohol on chlorophyll. Amorphous chlorophyll, which cannot be obtained

entirely free from impurities, when hydrolysed and subsequently methylated yields a trimethyl ester identical with that derived from crystalline chlorophyll; this ester when treated with potassium hydroxide is converted into the potassium salt of chlorophyllin, identical with the salt prepared directly from crystalline chlorophyll. The various preparations of the trimethyl ester contain two distinct substances: a blue compound and a green compound soluble with difficulty, which are separated by fractional precipitation and are similar in composition.

The action of alkalis on chlorophyll at 100–200° leads to the formation of two dicarboxylic acids, glaucophyllin and rhodophyllin, which are very similar both in chemical and physical properties, and can be separated only by the difference in their acidic properties.

The formation of rhodophyllin at 200° is accompanied by that of a monocarboxylic acid, phyllophyllin, whilst a second monocarboxylic acid, pyrrophyllin, is formed at 225–240°; the two compounds just mentioned are extremely similar, both chemically and optically; phyllophyllin is distinguished, however, by the solubility of the alkali and alkaline earth salts in ether. The monocarboxylic acids are less acidic than the dicarboxylic acids; thus, rhodophyllin may be separated from them by means of dilute ammonium hydroxide, in which phyllophyllin and pyrrophyllin are insoluble.

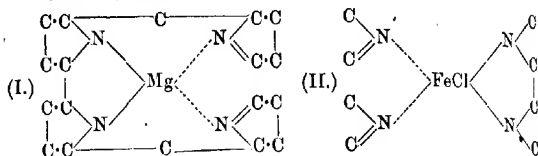
The phyllins are converted by acids into the corresponding porphyrins, compounds which do not contain magnesium. In order to emphasise this relationship between phyllins and porphyrins, it is proposed to change the name of the compound derived from rhodophyllin from *alloporphyrin* into *rhodoporphyrin* (compare Willstätter and Pfannenstiel, *loc. cit.*).

The dicarboxylic acids, glaucoporphyrin and rhodoporphyrin, are well-defined, crystalline compounds, soluble with difficulty and extremely similar in chemical properties; rhodoporphyrin is not identical with Tschirch's phylloporpuric acid, as suggested by Marchlewski (compare Abstr., 1908, i, 357). The monocarboxylic porphyrins, phylloporphyrin and pyrroporphyrin, resemble one another so closely that it is difficult to decide which of them corresponds with the substance described hitherto as phylloporphyrin, although it is very probable that the more basic of the two compounds (phylloporphyrin) is identical with the phylloporphyrin described by Marchlewski recently (*loc. cit.*); the phylloporphyrin of previous investigators was undoubtedly contaminated with other porphyrins.

The analysis of the complex substances described in this paper is rendered difficult owing to the stability of the compounds which they form with ether; however, from the results obtained it appears that the complex $[C_{31}H_{34}N_4Mg]$ is common to the phyllins, one, two, and three atoms of hydrogen being replaced by carboxyl in pyrrophyllin and phyllophyllin, glaucophyllin and rhodophyllin, chlorophyll, and the chlorophyllins respectively. The porphyrins are derived from the common nucleus $[C_{31}H_{35}N_4]$ in a similar manner.

As a result of the study of the phyllin esters and salts, particularly of those containing only one carboxyl group, it follows that carboxyl does not take part in the formation of the complex in the derivatives

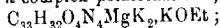
of chlorophyll, and that only the groups containing nitrogen are available for attachment to the magnesium atom; the centre of the complex may be represented by (I). Applying the same arguments in the case of hæmin, it follows that the iron in hæmin derivatives is combined in the manner indicated by (II) (compare Piloty and Merzbacher, Abstr., 1909, i, 857):



I. PHYLLINS.—Potassium chlorophyllin is a bluish-green powder, analyses of which indicate the atomic proportions $N_4:0.90Mg:2.60K$; when treated with methyl sulphate, it yields a mixture of two *chlorophyllin trimethyl* esters; the more soluble ester is a bluish-black, microscopic, crystalline powder, whilst the less soluble is a pale green powder. Both esters are decomposed by oxalic acid with the elimination of magnesium and formation of crystalline products containing oxalate; the solutions of the derivatives from the green and blue esters in chloroform are olive-brown and olive-green respectively.

Glaucophyllin, $C_{33}H_{34}O_4N_4Mg$, prepared by the action of a concentrated methyl-alcoholic solution of potassium hydroxide on chlorophyllin under pressure at a temperature not exceeding 140° , is purified by extracting the ethereal solution of the crude material with 0.004% ammonia, treating the aqueous solution with sodium dihydrogen phosphate, extracting with ether, and shaking the ethereal solution with a 0.02–0.05% solution of disodium hydrogen phosphate, in which glaucophyllin is insoluble; it crystallises in small, glistening prisms, which are green by transmitted light and greyish-blue by reflected light, and forms violet-blue solutions with an intense red fluorescence; the *potassium* salt, $C_{31}H_{32}N_4Mg(CO_2K)_2$, crystallises in microscopic, slender, violet prisms. Glaucophyllin is converted by alcoholic potassium hydroxide under pressure at 195 – 200° into rhodophyllin.

Rhodophyllin forms a complex *potassium* salt,



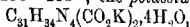
the normal potassium salt when treated with methyl sulphate yields the *dimethyl* ester, $C_{25}H_{38}O_4N_4Mg$, which crystallises in glistening prisms with a violet reflex and sinters at 310° .

Pyrophyllin, $C_{32}H_{34}O_2N_4Mg$, is best prepared by the action of alcoholic potassium hydroxide on rhodophyllin under pressure at 225 – 230° ; it crystallises in tufts of glistening plates, which are steel-blue or greyish-blue with a red tinge; recrystallisation from ether decreases the solubility of the compound without altering the composition; the ethereal solution at the same time changes from blue to red; the substance crystallises from absolute ether in glistening, reddish-violet prisms. The *pyridine* salt crystallises in glistening, violet leaflets; the *potassium* salt, $C_{31}H_{33}N_4Mg \cdot CO_2K$, crystallises in short, dark red prisms; the *calcium* salt, $(C_{32}H_{33}O_2N_4Mg)_2Ca$, forms

small, pale red needles; the *ammonium* salt forms brilliant red needles; the *sodium* salt crystallises in pale violet needles.

Phyllophyllin is formed in large quantity by the action of a methyl-alcoholic solution of potassium hydroxide on amorphous chlorophyll under pressure at 225–230°; it has not been isolated in a crystalline form, since it decomposes very readily; the ethereal solution is bluish-red with a red fluorescence; the *caesium* salt, $C_{31}H_{33}N_4Mg \cdot CO_2Cs$, crystallises in compact, glistening, bluish-violet prisms; the *potassium* salt ($1H_2O$) forms glistening, violet prisms; the *calcium* salt crystallises in bright red needles; the *magnesium* salt forms glistening, slender needles.

II. PORPHYRINS.—*Glauco porphyrin*, $C_{33}H_{30}O_4N_4$, crystallises in reddish-violet, microscopic needles; it sinters at 270° and is completely decomposed at 290–295°; the *potassium* salt,



crystallises in slender, pale brown leaflets; the *complex salt* with zinc acetate crystallises in glistening, violet prisms.

Rhodoporphyrin forms with zinc acetate an *additive compound*, crystallising in red needles, and with ferric chloride in glacial acetic acid a complex *iron* compound, obtained as a greyish-black, crystalline powder; the *dimethyl* ester, $C_{31}H_{34}N_4(CO_2Me)_2$, crystallises in glistening, reddish-brown prisms with a coppery reflex.

Pyroporphyrin, $C_{32}H_{30}O_2N_4$, crystallises in dark red, truncated prisms with a violet, metallic reflex; the solution in glacial acetic acid is red with a slight blue tinge. The *hydrochloride*, $C_{32}H_{30}O_2N_4 \cdot 2HCl$, crystallises in brown, slender, pointed prisms; the *hydrochloride*, $C_{32}H_{30}O_2N_4 \cdot 3HCl$, forms glistening, rhomboidal leaflets, which are brownish-red by transmitted light, violet by reflected light; the *potassium* salt, $C_{31}H_{35}N_4 \cdot CO_2K$, crystallises in reddish-brown prisms and rhomboidal leaflets; the *magnesium* salt was analysed; the *methyl* ester, $C_{31}H_{35}N_4 \cdot CO_2Me$, crystallises in long prisms; the *acetyl* compound, $C_{31}H_{35}N_4 \cdot CO_2Ac$, prepared by the action of hot acetic anhydride on pyroporphyrin, crystallises in rhomboidal leaflets and long prisms, which are red by transmitted light.

Phylloporphyrin crystallises in dark red, pointed prisms with a violet, metallic reflex; the solution in glacial acetic acid is dark violet-red; the *hydrochloride*, $C_{32}H_{30}O_2N_4 \cdot 3HCl$, crystallises in glistening, violet, four-sided prisms; the *magnesium* salt, $(C_{32}H_{30}O_2N_4)_2Mg$, is a brownish-red powder. The compound described by Schunck and Marchlewski as a zinc salt is a complex zinc compound.

The absorption spectra of alcoholic and ethereal solutions of glauco-phyllin, pyroporphyrin, phyllophyllin, pyroporphyrin, and phylloporphyrin, and of the hydrochlorides of the last two substances have been measured and are represented graphically. W. H. G.

The Tanning Process. JOHANN VON SCHROEDER (*Kolloidchem. Beihefte*, 1909, 1, 1–57).—The quantity of tannic acid adsorbed by unit weight of hide-powder is approximately constant; the amount which can be washed out again is less the longer the two have remained in contact. Water plays a certain part in the process, for hide-powder takes up no tannin from an alcoholic solution. A preliminary

treatment of the powder with formaldehyde largely prevents the subsequent adsorption of tannic acid. Gelatin resembles hide-powder in its relationship to tannic acid, if due allowance is made for the differences of physical condition of the two former substances under the circumstances of the experiment.

G. S. W.

Constitution of Hydroxymethylfurfuraldehyde. JAN J. BLANKSMA (*Chem. Weekblad*, 1909, 6, 1047—1053. Compare Kiermayer, *Abstr.*, 1896, i, 144; Fenton and Robinson, *Trans.*, 1909, 95, 1334).—Hydroxymethylfurfuraldehyde is formed by dehydration

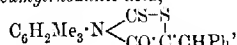
of chitose, and is the aldehyde, $\begin{matrix} \text{CH}=\text{C}(\text{COH}) \\ \text{CH}:\text{C}(\text{CH}_2\cdot\text{OH}) \end{matrix} > \text{O}$, corresponding with 2-hydroxymethylfuran-5-carboxylic acid, not with 4-hydroxy-2-methylfuran-5-carboxylic acid, as supposed by Kiermayer. The small proportion of furfuraldehyde obtained by heating certain pentoses is attributed to the partial decomposition of the hydroxymethylfurfuraldehyde first formed.

A. J. W.

Substituted Rhodanic Acids and their Aldehyde Condensation Products. VIII. LUDWIG KALUZA (*Monatsh.*, 1909, 30, 701—726. Compare Andreasch, *Abstr.*, 1908, i, 683, 684).—Rhodanic acids have been prepared from ψ -cumidine and isohexylamine.

3- ψ -Cumylrhodanic acid, $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{N} < \begin{matrix} \text{CS}-\text{S} \\ \text{CO}\cdot\text{CH}_2 \end{matrix}$, is obtained in the form of an oil from the corresponding ester, ethyl ψ -cumyldithiocarbamate, $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{NH}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, which is formed by the interaction of ethyl chloroacetate and ammonium cumyldithiocarbamate, and crystallises in short, transparent prisms, m. p. 84°.

5-Benzylidene-3- ψ -cumylrhodanic acid,



prepared by condensation with benzaldehyde, is a citron-yellow oil, crystallising in citron-yellow needles, m. p. 127°.

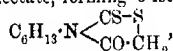
5-mp-Methylenedioxybenzylidene-3- ψ -cumylrhodanic acid, similarly prepared by condensation with piperonal, is a coarse, chrome-yellow powder, consisting of prismatic needles, m. p. 188°.

5-m-Nitrobenzylidene-3- ψ -cumylrhodanic acid forms a sulphur-yellow, crystalline powder, m. p. 224°. The corresponding 5-p-nitrobenzylidene-3- ψ -cumylrhodanic acid is a dark yellow powder, which becomes brown at 190°, sinters at 200°, m. p. 230°.

5-p-Dimethylaminobenzylidene-3- ψ -cumylrhodanic acid forms splendid blood-red, stout needles, m. p. 192°. The alcoholic solution is a deep chrome-yellow when dilute, blood-red when concentrated.

5-p-Methoxybenzylidene-3- ψ -cumylrhodanic acid forms glistening, chrome-yellow, microscopic prisms, m. p. 174°.

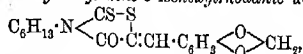
isoHexylamine isohexyldithiocarbamate, $\text{C}_6\text{H}_{13}\cdot\text{NH}\cdot\text{CS}\cdot\text{S}\cdot\text{NH}\cdot\text{C}_6\text{H}_{13}$, prepared by the interaction of isohexylamine and carbon disulphide, forms colourless, regular, prismatic crystals, m. p. 85°. It reacts with ethyl monochloroacetate, forming 3-isohexylrhodanic acid,



a clear, fluid, transparent, light yellow oil, b. p. 199—200°/11 mm.

5-Benzylidene-3-isohexylrhodanic acid, $\text{C}_6\text{H}_{13}\cdot\text{N} \begin{smallmatrix} \text{CS-S} \\ \text{CO}\cdot\text{C}\cdot\text{CHPh} \end{smallmatrix}$ forms long, lustrous, bright yellow needles, m. p. 87° . *5-m-Nitrobenzylidene-3-isohexylrhodanic acid* crystallises in light yellow, glistening plates, m. p. $166-167^\circ$. *5-p-Nitrobenzylidene-3-isohexylrhodanic acid* is a brownish-yellow, microcrystalline powder, m. p. $130-131^\circ$.

5-mp-Methylenedioxybenzylidene-3-isohexylrhodanic acid,

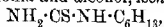


consists of golden-yellow, lustrous needles with a blue reflex, m. p. 98° . *5-p-Dimethylaminobenzylidene-3-isohexylrhodanic acid* forms a matted mass of lustrous, red needles with a blue reflex, m. p. 140° . *5-o-Hydroxybenzylidene-3-isohexylrhodanic acid* crystallises in orange-yellow, short, matted needles, m. p. $170-172^\circ$. With sodium hydroxide, bluish-red crystals of the sodium salt are formed. It dyes wool and silk bright yellow.

5-p-Methoxybenzylidene-3-isohexylrhodanic acid forms long, chrome-yellow, lustrous needles, m. p. 85° .

5-Cinnamylene-3-isohexylrhodanic acid forms golden, crystalline masses, consisting of regular, rectangular, microscopic cubes, m. p. $129-131^\circ$.

isoHexylthiocarbimide, $\text{SC}\cdot\text{N}\cdot[\text{CH}_2]_3\cdot\text{CHMe}_2$, prepared by the interaction of ethyl chlorocarbamate and isohexylamine isohexyldithiocarbamate, is a faintly yellow coloured, clear, mobile oil, with a not unpleasant odour, b. p. $120-121^\circ/18$ mm., $208-209^\circ/760$ mm. When treated with ammonia and alcohol, *isohexylthiocarbamide*,



is formed, crystallising in thin, rectangular plates, m. p. 62° , of fatty lustre. *Düisohexylthiocarbamide*, $\text{CS}(\text{NH}\cdot\text{C}_6\text{H}_{13/2})_2$ forms thin, silvery-glistening, rhombic plates, m. p. 46° .

isoHexylthioparabanic acid, $\text{CS} \begin{smallmatrix} \text{N}(\text{C}_6\text{H}_{13})\cdot\text{CO} \\ \text{NH} \text{---} \text{CO} \end{smallmatrix}$ prepared by the interaction of *isohexylthiocarbamide* and cyanogen, crystallises in light yellow, thin plates, m. p. 110° . By the action of silver nitrate it is converted into *isohexylparabanic acid*, $\text{CO} \begin{smallmatrix} \text{N}(\text{C}_6\text{H}_{13})\cdot\text{CO} \\ \text{NH} \text{---} \text{CO} \end{smallmatrix}$ which forms long, colourless, silky, matted needles, m. p. 76° . *Düisohexylthioparabanic acid* crystallises in long, flat, citron-yellow needles, m. p. 40° . *Düisohexylparabanic acid* was only obtained in the form of a syrup.

E. F. A.

Additive Products of Halogen Acetamide with Atropine.
ALFRED EINHORN and MAXIMILIAN GÖTTLER (*Ber.*, 1909, 42, 4853-4854).—The additive product of atropine with bromoacetonitrile has been shown by Braun (*Abstr.*, 1908, i, 675) to have lost the specific pharmacological action of atropine; this is not, however, the case as regards the compounds with the halogen acetamides.

Atropinechloroacetamide forms a flocculent precipitate of lustrous

plates, m. p. 204—205° (decomp.). *Atropinebromoacetamide* forms bunches of matted needles, m. p. 204—205°; *atropineiodoacetamide* forms an indefinitely crystalline aggregate, m. p. 203—204° (decomp.).
E. F. A.

Caffeine. A. J. ULTÉE (*Chem. Weekblad*, 1910, 7, 32—34).—Additive products of caffeine with pyrogallol and phloroglucinol respectively have been prepared; they contain equimolecular proportions of their constituents. *Caffeine-pyrogallol*, $C_8H_{10}O_2N_4 \cdot C_3H_2O_3 \cdot 4H_2O$, forms acicular crystals, m. p. 70°. The water of crystallisation is given off in a vacuum desiccator over sulphuric acid. The whole of the caffeine can be extracted by chloroform.

Caffeine-phloroglucinol, $C_8H_{10}O_2N_4 \cdot C_6H_2O_3 \cdot 2H_2O$, forms ill-defined crystals, m. p. about 185°.

Theobromine is rapidly converted into caffeine by the action of methyl sulphate.
A. J. W.

Action of Grignard's Solutions on β -Cinchonine- and β -Quinine-ethiodides. MARTIN FREUND and FRITZ MAYER (*Ber*, 1909, 42, 4724—4728).—The β -ethiodide of cinchonine (Skraup and Norwall, *Abstr.*, 1894, i, 391) has a constitution analogous to that of quinoline methiodide, and reacts with Grignard's reagent in much the same manner, yielding 1:2-diethyl-1:2-dihydrocinchonine and 2-phenyl-1-ethyl-1:2-dihydrocinchonine, $C_6H_5 \cdot \text{NEt} \cdot \text{CH} \cdot \text{Et} \cdot \text{CH} \cdot \text{C}_6H_4 \cdot \text{ON} \cdot \text{C}_6H_4$. Quinine β -methiodide reacts in the same manner.

1:2-Diethyl-1:2-dihydrocinchonine, $C_{23}H_{32}ON_2$, crystallises from alcohol in needles, which sinter at 173° and are completely molten at 187°. Its salts do not crystallise, and the yield of the base is poor.

2-Phenyl-1-ethyl-1:2-dihydrocinchonine, $C_{27}H_{32}ON_2$, crystallises from dilute alcohol in slender needles, and has m. p. 135° after softening at 120°. The *hydriodide*, $C_{27}H_{32}ON_2HI$, crystallises in plates, which decompose at 263°. The corresponding *hydrochloride* and *hydrobromide* have been prepared.

The product $C_{24}H_{34}O_3N_2$, obtained from quinine- β -ethiodide and ethyl magnesium bromide, could not be obtained in a crystalline form. The physiological properties of the products have been studied.
J. J. S.

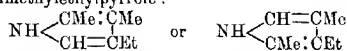
Action of Chloroform on 2:5-Dimethylpyrrole. GIUSEPPE PLANCHER and U. PONTI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 469—474).—The action of chloroform on 2:5-dimethylpyrrole in presence of alcoholic potassium hydroxide yields 2:5-dimethylpyrrole-3-aldehyde, 2-(or 3-)dichloromethyl-2:5-dimethylpyrrolene, and 3-chloro-2:6-dimethylpyridine (compare Bocchi, *Abstr.*, 1900, i, 357).

2:5-Dimethylpyrrole-3-aldehyde, $\text{NH} \cdot \text{C}(\text{Me})_2 \cdot \text{CH} \cdot \text{CHO}$, forms colourless scales or mammillary crystals, m. p. 144°, and does not reduce Fehling's solution. Its *p*-nitrophenylhydrazone, $C_{13}H_{11}O_3N_4$, forms garnet-red crystals with metallic lustre, m. p. 234°. With

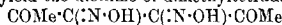
β -naphthylamine (1 mol.) and pyruvic acid (1 mol.) in alcoholic solution, the aldehyde (1 mol.) gives the corresponding *naphthacinchoninic acid*, m. p. 267°.

2:5-Dimethyl-(1)-dichloromethylpyrroline, $\text{N} \begin{smallmatrix} \text{CMe} \\ \text{CMe} \end{smallmatrix} \begin{smallmatrix} \text{CH} \\ \text{CHCl}_2 \end{smallmatrix}$ or $\text{N} \begin{smallmatrix} \text{CMe} \cdot \text{CH} \\ \text{CMe} \cdot \text{CH} \cdot \text{CHCl}_2 \end{smallmatrix}$, is a heavy, colourless liquid having a basic odour resembling that of burnt almonds, and yields a *picrate*, $\text{C}_7\text{H}_5\text{NCl}_2 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, separating in pale yellow, rhombic scales, m. p. 144°. T. H. P.

Constitution of Hæmopyrrole and of Hæmopyrrole-carboxylic Acid. OSCAR PILOTY and E. QUITMANN (*Ber.*, 1909, 42, 4693—4703).—Pure hæmopyrrole can be obtained by carefully fractionating the crude product prepared by the method described previously (*Abstr.*, 1909, i, 539). It has b. p. 114—115°/35 mm., m. p. 39°, and forms flat, quadratic plates. When fused, it forms a colourless oil with a pale fluorescence. The potassium derivative forms a colourless, crystalline powder, and the *picrate* has m. p. 108.5°. The constitution of hæmopyrrole has been settled by the action of nitrous acid. 2:4-Dimethylpyrrole (Knorr, *Abstr.*, 1884, 1368), when treated with nitrous acid, yields the oxime of citraconimide, the 2-methyl group being eliminated. Pure hæmopyrrole and nitrous acid yield the oxime of methylethylmaleinimide, and as in this reaction a 2-methyl group is probably eliminated, hæmopyrrole should be a dimethylethylpyrrole:

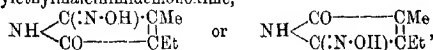


2:5-Dimethylpyrrole (Paal, *Abstr.*, 1885, 1206; Knorr, *ibid.*, 995) and nitrous acid yield the dioxime of dimethyltetraketone,



(compare Thal, *Abstr.*, 1892, 1074).

Methylethylmaleinimidemonoxime,



crystallises from water in colourless prisms, and has m. p. 201°. It is identical with the compound described previously (*Abstr.*, 1909, i, 539) as melting at 206—207°. When hydrolysed with dilute sulphuric acid it yields methylethylmaleinimide.

Citraconimidemonoxime, $\text{NH} \begin{smallmatrix} \text{CO} \text{---} \text{CMe} \\ \text{C}(\text{N} \cdot \text{OH}) \cdot \text{CH} \end{smallmatrix}$, forms small, colourless prisms, m. p. 223—224°, and when hydrolysed yields citraconic acid.

The oxime of hæmatic acid (*loc. cit.*, 540) when hydrolysed yields hæmatic acid.

It has not been found possible to decompose hæmopyrrole by means of hydroxylamine, although both 2:4- and 2:5-dimethylpyrroles are decomposed by this reagent (Ciamician and Zanetti, *Abstr.*, 1890, 264, 1155).

A number of products are formed by reducing hæmatoporphyrin VOL. XXVIII. i.

with hydriodic acid and phosphorus; among these is an oil of low b. p., which yields a *picrate*, $C_{14}H_{18}O_7N_3$, m. p. 143—145°.

J. J. S.

New Cinchonic Acid Syntheses. ROBERT SCHIFF (*Ber.*, 1909, 42, 4918. Compare Borsche, *Abstr.*, 1909, i, 955).—A claim for priority.

R. V. S.

Quinoline Derivatives. ALFRED EINHORN (*Ber.*, 1909, 42, 4854—4856).—[With RICHARD FEIDELMANN.]—*Ethyl quinoline-6-carboxylate hydrochloride* is prepared by boiling a suspension of the hydrochloride of *p*-quinolinecarboxylic acid in alcohol containing hydrogen chloride; it crystallises in bunches of needles, m. p. 210° (decomp.). The free acid forms matted needles, m. p. 50°.

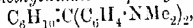
The *hydrochloride of diethylaminoethyl quinoline-6-carboxylate*, $C_{20}H_{26}N \cdot CO \cdot O \cdot CH_2 \cdot CH_2 \cdot NEt_2 \cdot HCl$, prepared by the action of diethylaminoethanol on quinoline-6-carboxylic acid, is a faintly yellow-coloured, microcrystalline substance, m. p. 180°.

[With MAXIMILIAN GÖTTLER.]—*Quinoline-6-acetamide*, $C_9H_7N \cdot CH_2 \cdot CO \cdot NH_2$

crystallises from water in lustrous, orange-hued, refractive plates, or from alcohol in yellow needles, decomp. 250°; the solution has a green fluorescence.

E. F. A.

Action of Magnesium cyclohexyl Bromide on Tetramethyldiaminobenzophenone. ANDRÉ WAHL and ANDRÉ MEYER (*Bull. Soc. chim.*, 1910, [iv], 7, 28—31. Compare *Abstr.*, 1908, i, 890).—The authors have repeated the experiments of Schmidlin and Escher (*Abstr.*, 1908, i, 163), and have succeeded in obtaining a small quantity of *cyclohexyldenetetramethyldiaminodiphenylmethane*,



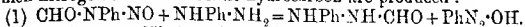
m. p. 144—145°.

This was obtained by treating an ethereal solution of magnesium *cyclohexyl* bromide with tetramethyldiaminobenzophenone and adding water. The precipitate, after the removal of magnesium compounds, consists mainly of unaltered ketone, from which the substance sought was separated by tedious fractionation from solutions in a mixture of acetone and ether, in which it is readily soluble. It crystallises in bright yellow prisms, and when dissolved in acetic acid gives with mild oxidising agents, such as lead peroxide, an intensely blue coloration, resembling that similarly obtained by Lemoult (*Abstr.*, 1909, i, 836) with the *pp*-dialkyl derivatives of *α*-diphenylethylene. Since this new substance gives this reaction, it follows that the development of this blue dye is not due, as Lemoult supposed, to the specific influence of a characteristic hydrogen atom, since this is absent in the new substance.

T. A. H.

Reaction of Nitrosoamides with Phenylhydrazine. RICHARD WILLSTATTER and ARTHUR STOLL (*Ber.*, 1909, 42, 4872—4877).—When nitrosoformanilide reacts with phenylhydrazine (more than 2 mols.) in benzene at 0°, nitrogen is evolved and *s*-formylphenyl

hydrazide is produced. This is not an instance of the migration of an acyl group, because nitrosoformo-*p*-toluidide and phenylhydrazine also yield *s*-formylphenylhydrazide, and nitrosoformanilide and *p*-tolylhydrazine yield *s*-formyl-*p*-tolylhydrazide. The reaction consists, therefore, in an acylation of the hydrazine by the nitrosoacylamide, which thus is converted into a diazo-compound; this, reacting with a second molecule of the hydrazine, forms a diazohydrazide, by the decomposition of which nitrogen and an aromatic hydrocarbon are produced:



The diazohydrazides can be isolated under suitable conditions. Nitrosoformanilide is very slowly introduced into a well-cooled dilute benzene solution of phenylhydrazine, the formylphenylhydrazine is removed, and the last portions are precipitated by the addition of light petroleum; the filtrate is evaporated, whereby a residue of diazobenzenephylhydrazide, m. p. 71°, is obtained.

In a similar way, phenylhydrazine reacts with nitrosoacetanilide, nitrosophenylcarbamide, and nitrosomethylurethane, forming *s*-acetylphenylhydrazide, phenylsemicarbazide, and ethyl phenylcarbazinate respectively.

Other nitroso-compounds lose their nitroso-group by treatment with phenylhydrazine; nitrosophenylurethane, nitro-obenzanilide, diphenylnitrosoamine, and phenylethylnitrosoamine are converted into phenylurethane, benzanilide, diphenylamine, and phenylethylamine respectively; nitrous oxide is evolved in the last two cases.

Nitrosoformanilide and aniline in alcohol solution yield diazoaminobenzene and formanilide, the reaction following a course similar to the first-mentioned above. C. S.

New Phototropic Substances. II. MAURICE PADOA and F. GRAZIANI (*Atti R. Accad. Lincei*, 1909, [v], 13, ii, 559—564. Compare Abstr., 1909, i, 964).—The authors have obtained the following further results:

Cinnamaldehydophenylhydrazone, m. p. 171° (Fischer, Abstr., 1884, 1150, found 168°), is slightly phototropic.

Piperonaldehydophenylhydrazone, m. p. 106° (Rudolph, Abstr., 1889, 251, found 102—103°), is not phototropic.

p-Tolualdehydophenylhydrazone, $\text{NHPh} \cdot \text{N} \cdot \text{CH} \cdot \text{C}_6\text{H}_4\text{Me}$, forms a yellow, crystalline powder, m. p. 121°, and is feebly phototropic.

With the *m*-tolylhydrazones, phototropy is observed, but less frequently and less intensely than with the *p*-tolylhydrazones; the corresponding ortho-compounds are not phototropic.

Benzaldehyde-*m*-tolylhydrazone, $\text{C}_6\text{H}_4\text{Me} \cdot \text{N}_2\text{H} \cdot \text{CHPh}$, separates in slender, whitish-yellow needles, m. p. 100°, and exhibits phototropic properties.

Anisaldehyde-*m*-tolylhydrazone, $\text{C}_6\text{H}_4\text{Me} \cdot \text{N}_2\text{H} \cdot \text{CH} \cdot \text{C}_6\text{H}_4\text{OMe}$, forms a yellow, crystalline powder, m. p. 111°, and is not phototropic.

Cuminaldehyde-*m*-tolylhydrazone, $\text{C}_6\text{H}_4\text{Me} \cdot \text{N}_2\text{H} \cdot \text{CH} \cdot \text{C}_6\text{H}_4\text{CHMe}_2$, crystallises in yellowish-white needles, m. p. 136°, and is faintly phototropic.

Cinnamaldehyde-m-tolylhydrazone, $C_9H_7Me \cdot N_2H \cdot CH \cdot CH \cdot CHPh$, forms a yellow, crystalline powder, m. p. 131° , and is feebly phototropic.

Piperonaldehyde-m-tolylhydrazone, $C_8H_4Me \cdot N_2H \cdot CH \cdot C_6H_3O_2 \cdot CH$, forms canary-yellow needles, m. p. 131° , and is distinctly phototropic.

p-Tolualdehyde-m-tolylhydrazone, $C_8H_4Me \cdot N_2H \cdot CH \cdot C_6H_4Me$, separates as an intensely yellow, crystalline powder, m. p. 121° , and is not phototropic.

Benzaldehyde-*o*-tolylhydrazone becomes coloured in the air even in the dark, but much more slowly than is the case with a phototropic compound (compare Reutt and Pawlewski, Abstr., 1904, i, 99). Such coloration appears to be favoured by moisture.

Anisaldehyde-o-tolylhydrazone crystallises in shining, white scales, m. p. 94° , and is not phototropic, but it softens in the air, giving ultimately a dark red syrup.

Cuminaldehyde-o-tolylhydrazone forms canary-yellow, shining scales, m. p. 91° , and is not phototropic; it readily changes in the air, its colour becoming red and its m. p. being lowered.

Piperonaldehyde-o-tolylhydrazone forms shining, yellow scales, m. p. 87° , and is not phototropic.

p-Tolualdehyde-o-tolylhydrazone crystallises in pale yellow scales, m. p. 109° , and is not phototropic; it readily becomes red in the air, especially in moist air. T. H. P.

Synthesis of Polypeptides. XXXII. Derivatives of L-Proline and of Phenylalanine. EMIL FISCHER and ANDRÁS LUNIAK (*Ber.*, 1909, 42, 4752—4759. Compare Fischer and Suzuki, Abstr., 1904, i, 771; Fischer and Reif, *ibid.*, 1908, i, 1007).—*L-Prolyl-l-phenylalanine*, $\begin{matrix} CH_2 \cdot CH \\ | \\ CH_2 \cdot NH \end{matrix} > CH \cdot CO \cdot NH \cdot CH < \begin{matrix} CO_2H \\ | \\ CH_2 \cdot Ph \end{matrix}$, prepared by

condensing *l*-prolyl chloride with *l*-phenylalanine ethyl ester and hydrolysing the resulting product with barium hydroxide, is identical with the dipeptide obtained by Osborne and Clapp (Abstr., 1908, i, 115) by the hydrolysis of gliadin with sulphuric acid.

The dipeptide is decomposed by pancreatin in a sodium carbonate solution at 36° during the course of forty-eight hours, and yields *l*-proline and *l*-phenylalanine.

L-Prolyl-d-phenylalanine, $C_{14}H_{18}O_3N_2 \cdot H_2O$, has also been prepared synthetically; it forms small, colourless prisms, has m. p. 223° (corr. decomp.), is more soluble in water than the isomeride, and has a bitter taste.

The copper salt, $C_{14}H_{16}O_3N_2Cu \cdot 2H_2O$, forms dark blue, microscopic prisms. J. J. S.

Aminopyrrolidone Derivatives from Mesityl Oxide and Aminolactones from Diacetone Alcohol. MORITZ KOHN and FRIEDRICH BUM (*Monatsh.*, 1909, 30, 729—743. Compare Abstr., 1908, i, 819, 829).—A continuation of previous work. The 4-methylamino-1:2:2:4-dimethyl-5-pyrrolidone, $C_9H_{18}ON$, is now obtained as a colourless, crystalline mass, m. p. 32° , b. p. 121 — $129^\circ/11$ mm.

It reacts with ethylene oxide forming a colourless, amorphous compound, $\text{CMe}_2 \begin{smallmatrix} \text{NMe} \cdot \text{CO} \\ \text{CH}_2 \end{smallmatrix} \text{CMe} \cdot \text{NMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$; this yields a characteristic aurichloride, $\text{C}_{11}\text{H}_{22}\text{O}_2\text{N}_2 \cdot 2\text{HAuCl}_4 + \text{H}_2\text{O}$, decomp. 167° . The compound forms an additive product with methyl iodide, which was converted into the methochloride and analysed as the platinumchloride, $\text{C}_{11}\text{H}_{22}\text{O}_2\text{N}_2 \cdot \text{HCl} \cdot \text{CH}_3\text{Cl} \cdot \text{PtCl}_4$, which crystallises in orange tablets.

4-Ethylamino-2:2:3-trimethyl-1-ethyl-5-pyrrolidone, $\text{C}_{11}\text{H}_{22}\text{ON}_2$, is a viscid oil, b. p. $127-131^\circ/13-14$ mm. The compound formed on interaction with ethylene oxide did not crystallise or yield crystalline salts, but was analysed in the form of the platinumchloride of the methochloride, $\text{C}_{13}\text{H}_{26}\text{O}_2\text{N}_2 \cdot \text{HCl} \cdot \text{CH}_3\text{Cl} \cdot \text{PtCl}_4$.

4-Amino-5-keto-2:2:4-trimethyltetrahydrofuran forms a yellow picrate, m. p. $145-146^\circ$. The picrate of the corresponding 4-methylamino-compound crystallises in orange-yellow needles, m. p. 179° . The corresponding 4-dimethylamino-compound has b. p. $111^\circ/11$ mm., and yields a picrate, m. p. 175° , crystallising in well-formed citron-yellow needles.

4-Ethylamino-5-keto-2:2:4-trimethyltetrahydrofuran, synthesised from diacetone alcohol, ethylamine hydrochloride, and potassium cyanide, is a colourless, mobile liquid, b. p. $138-140^\circ/15$ mm. The phenylcarbamide, $\text{C}_{16}\text{H}_{22}\text{O}_2\text{N}_2\text{S}$, forms a colourless, sandy powder, m. p. 168° . The lactone further interacts with nitrous acid, forming a

nitroso-derivative, $\text{CMe}_2 \begin{smallmatrix} \text{O} \cdot \text{CO} \\ \text{CH}_2 \end{smallmatrix} \text{CMe} \cdot \text{N}(\text{NO})\text{C}_2\text{H}_5$, which crystallises in colourless needles, m. p. 67° .

E. F. A.

Action of Formaldehyde and Secondary Bases on Isatin. ALFRED EINHORN and MAXIMILIAN GÜTTLER (*Ber.*, 1909, 42, 4850-4852).—By the action of formaldehyde and secondary bases on isatin, two molecules of water are eliminated and condensation products formed, which are considered to be derived from the lactam formula: $\text{CO} \begin{smallmatrix} \text{CO} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{N} \cdot \text{CH}_2 \cdot \text{NRR}'$.

ω -Diethylaminomethylisatin forms short, red crystals, aggregated in large clusters, m. p. $77-78^\circ$. ω -Phenylethylaminomethylisatin crystallises in deep red, reniform aggregates of thin plates, m. p. 98° .

E. F. A.

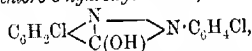
Synthesis of 5:7:5':7'-Tetrabromoindigotin and 5:7:5':7'-Tetrachloroindigotin. NEGOÏTA DANAILA (*Compt. rend.*, 1909, 149, 1383-1386. Compare *Abstr.*, 1908, i, 468, 798).—The constitution of the tetrabromogen derivatives of indigotin follows from the synthesis of these compounds by the reduction of 5:7-dibromoisatin chloride and 5:7-dichloroisatin chloride with hydrogen iodide (compare Grandmougin, this vol., i, 74).

Details of the absorption spectra of the compounds are given.

W. O. W.

Constitution of Indirubin. LOUIS C. MAILLARD (*Bull. Soc. chim.*, 1909, [iv], 5, 1153—1158).—In a previous paper (Abstr., 1902, i, 371) the author has shown that indigotin dissolved in chloroform to which hydrochloric acid has been added, slowly passes into indirubin, and on this ground has suggested (Abstr., 1903, i, 761) new formulæ for indigotin and indirubin, in which these are represented as polymerides, $C_{32}H_{20}O_4N_4$, of a supposed hemi-indigotin, $C_{16}H_{10}O_2N_2$. The evidence brought forward by Beckmann and Gabel (Abstr., 1906, i, 900) and Vaubel (*ibid.*, 989) that indigotin has the formula $C_{16}H_{10}O_2N_2$ is discounted by the fact that it was not obtained by physical determinations, but this objection does not apply to that derived from Wahl and Bagard's new synthesis of indirubin (Abstr., 1909, i, 300), which, in the opinion of these authors, supports the simple formula generally accepted for this substance. In this connexion the author points out that this acceptance implies (1) that mere standing of indigotin in acidified chloroform is sufficient to rotate the pyrrole nucleus from the α - to the β -position, or (2) that throughout the course of the new synthesis the oxindole nucleus does not remain unchanged in position. T. A. H.

3-Hydroxyindazolyl Derivatives. PAUL FREUNDLER (*Compt. rend.*, 1909, 149, 1135—1137. Compare Abstr., 1906, i, 544; 1907, i, 158; 1909, i, 145).—*o*-Benzeneazobenzoic acid is obtained in 70–80% yield by condensing *o*-nitrosobenzoic acid with aniline. By treating this with phosphorus pentachloride and oxidising the product, a mixture of *o*-benzeneazochlorobenzoic acids is obtained, which, on treatment with phosphorus pentachloride, yields only 4:6-dichloro-3-hydroxyindazole, m. p. 187°. By treating *o*-benzeneazo-*p*-chlorobenzoic acid in the same way, *trichloro-3-hydroxyindazole*,



has been prepared; it forms needles, m. p. 209–210°.

The formation of a mixture of monochloro-derivatives when phosphorus pentachloride acts on *o*-carboxylic azo-compounds appears to indicate that the formation of chlorohydroxyindazoles is not due to direct chlorination. *Azobenzene-o-carboxylic acid*, prepared by condensing phenylhydroxylamine with *o*-nitrosobenzoic acid, crystallises in yellow prisms, m. p. 118°.

Hubner's 3:5-dibromoanthranilic acid does not condense with nitrobenzene. The *acetyl* derivative of the acid has m. p. 221° (decomp); the *methyl* ester forms spangles, m. p. 91°. W. O. W.

Pyrimidines. XLIX. Thio-derivatives of Thymine and the Preparation of Thymine. HENRY L. WHEELER and DAVID F. McFARLAND [and, in part, WALTER F. STOREY] (*Amer. Chem. J.*, 1910, 43, 19–36).—Wheeler and Liddle (Abstr., 1903, i, 60) have shown that in the preparation of uracil a larger yield is obtained by condensing ethyl sodioformylacetate with thiocarbamide than by condensing it with ψ -ethylthiocarbamide. Experiments have therefore been carried out in order to ascertain whether the preparation of thymine could be improved in a similar manner. It has been found that when ethyl

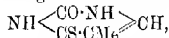
sodioformylpropionate is condensed with thiocarbamide in aqueous solution, the yield of 2-thiothymine is only about one-half of that obtained by the use of ψ -ethylthiocarbamide, but that if the reaction is carried out in alcoholic solution, a much larger yield is obtained, amounting to about 22.6% of the calculated quantity, and nearly identical with that furnished by the ψ -ethylthiocarbamide condensation.

2-Thiothymine, $\text{NH} \begin{smallmatrix} \text{CS-NH} \\ \text{CO-CMe} \end{smallmatrix} \text{CH}$, forms fairly stout prisms, is soluble in water at 20° to the extent of 0.133%, and is readily converted into thymine by heating its aqueous solution with chloroacetic acid. Thymine is soluble in water at 23° to the extent of 0.303%. 2-Thiothymine has a more pronounced acid character than thymine; its sodium, potassium, and copper salts are described.

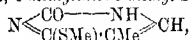
2-Benzylthiol-5-methyl-6-pyrimidone, $\text{NH} \begin{smallmatrix} \text{C(S-CH}_2\text{Ph):N} \\ \text{CO} \text{---} \text{CMe} \end{smallmatrix} \text{CH}$, m. p. 204–205°, obtained by the action of benzyl chloride on the potassium salt of 2-thiothymine, forms colourless needles.

6-Thio-2-ethylthiol-5-methylpyrimidine, $\text{NH} \begin{smallmatrix} \text{C(SEt):N} \\ \text{CS-CMe} \end{smallmatrix} \text{CH}$, m. p. 181°, obtained by warming 6-chloro-2-ethylthiol-5-methylpyrimidine (Wheeler and Johnson, Abstr., 1904, i, 621) with a solution of potassium hydrogen sulphide, crystallises in prismatic needles, and, when heated at 215° in a current of hydrogen chloride, is converted into 2:6-dithiothymine, $\text{NH} \begin{smallmatrix} \text{CS-NH} \\ \text{CS-CMe} \end{smallmatrix} \text{CH}$, m. p. 281° (decomp.), which forms small, bright yellow needles.

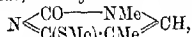
When 6-thio-2-ethylthiol-5-methylpyrimidine is boiled with concentrated hydrochloric acid for one and a half hours, it is converted into thymine, but, on less vigorous treatment, 6-thiothymine,



m. p. 330° (decomp.), is produced, which forms bright yellow, silky needles. By the action of methyl iodide on 6-thiothymine in presence of potassium hydroxide, 6-methylthiol-5-methyl-2-pyrimidone,



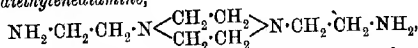
m. p. 205–211°, is obtained, which forms pale yellow, prismatic needles. When this substance is heated with methyl iodide in presence of potassium hydroxide, 6-methylthiol-3:5-dimethyl-2-pyrimidone,



m. p. 83°, is obtained, which forms white, prismatic needles, and, when boiled with concentrated hydrochloric acid, is converted into 3-methylthymine (Johnson and Clapp, Abstr., 1908, i, 835). E. G.

Derivatives of Piperazine. ANTOINE P. N. FRANCHIMONT and E. KRAMER (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 452–454). —Van Dorp (Abstr., 1909, i, 327), who prepared piperazinediacetic acid together with the corresponding diamide and dinitrile, failed to esterify the acid; this has now been effected. The acid forms a compound with sulphuric acid, and, when this is heated with excess of

this acid and alcohol, the crystalline compound of sulphuric acid with the ester is obtained. The ester is freed by treatment with bases under a layer of ether or benzene. The methyl ester is a colourless substance, m. p. 63°; the ethyl ester, m. p. 47.5°, is also crystalline. Being tertiary amines, both not only combine with acids, but also with methyl iodide, but of this they only unite with one molecule. The compound obtained in this way from the methyl ester has m. p. 144–145°, that from the ethyl ester, m. p. 143°. The compound *piperazinediethylenediamine*,



was obtained by reduction of the dinitrile by means of sodium and alcohol. The anhydrous compound, m. p. 40–41°, is hygroscopic, yields with water a crystalline compound, m. p. 63°, and with 4HCl a non-hygroscopic, crystalline *hydrochloride*. The *picrate* and *oxalate* form yellow and colourless crystals respectively; the *picryl* derivative is crystalline and decomposes at 238°, and a *benzoyl* derivative was obtained. Similar derivatives of the lower homologue of the above, namely, *piperazinedimethylenediamine*, were prepared. This compound could not be obtained from the acetamide by Hoffmann's method, so that it was necessary to resort to the sodium and alcohol reduction of *piperazinediformonitrile*. This substance, prepared from bromo-cyanogen and piperazine in aqueous solution with addition of alkali, crystallises in leaflets, m. p. 168°, and combines neither with methyl iodide, benzene, nor oxalic acid. G. S. W.

Ketochlorides and Quinones of Heterocyclic Compounds and Their Transformation Products. III. Ketochlorides and Quinones of Phenyl- ψ -aziminobenzene [2:1:3-Benzotriazole]. THEODOR ZINCKE and E. SCHARFF [*Annalen*, 1909, 370, 297–314].—A preliminary note of this investigation has appeared already (compare Zincke and Petermann, Abstr., 1899, i, 135). A complete parallelism is shown to exist between phenyl- ψ -aziminobenzene [2:1:3-benzotriazole] and phenylaziminobenzene [1:2:3-benzotriazole], the different structure of the nitrogen ring having no marked influence on the chemical properties (compare Zincke, Stoffel, and Petermann, Abstr., 1900, i, 524; Zincke and Petermann, Abstr., 1901, i, 104).

5-Amino-2-phenyl-2:1:3-benzotriazole has m. p. 183° (compare Kehrman and Messinger, Abstr., 1892, 889); the *sulphate* and *hydrochloride* crystallise in colourless needles; the *acetyl* derivative, $\text{C}_{12}\text{H}_{12}\text{ON}_4$, crystallises in faintly pink, silky, slender needles, m. p. 192°.

6-Chloro-5-nitro-2-phenyl-2:1:3-benzotriazole, $\text{NPh} \begin{array}{c} \text{N}\cdot\text{C}\cdot\text{CH}\cdot\text{C}\cdot\text{NO}_2 \\ \text{N}\cdot\text{C}\cdot\text{CH}\cdot\text{C}\cdot\text{Cl} \end{array}$,

is prepared by boiling a solution of 1:3-dichloro-4:6-dinitrobenzene in 96% alcohol with phenylhydrazine and crystalline sodium acetate; it forms pale yellow needles, m. p. 196°, and when reduced with hydrochloric acid and tin yields the corresponding *amino*-compound, $\text{C}_{12}\text{H}_9\text{N}_4\text{Cl}$, small, glistening, brownish-yellow leaflets and needles,

m. p. 221—222°, the *acetyl* derivative of which crystallises in slender, white needles, m. p. 221°.

4 : 5 : 7 : 7-Pentachloro-6-keto-2-phenyltetrahydro-2 : 1 : 3-benzotriazole, $\text{NPh} \begin{smallmatrix} \text{N} \cdot \text{C} \cdot \text{CO} \\ | \quad | \\ \text{N} \cdot \text{C} \cdot \text{CHCl} \cdot \text{CCl}_2 \end{smallmatrix}$, is formed together with small quantities of the

corresponding *hexachloroketochloride* by the action of chlorine on the stannichloride of either of the amino-compounds just described; it forms stout, yellowish-green, monoclinic crystals, m. p. 128°, and when reduced yields a mixture of the corresponding *dichlorohydroxy-* and *trichlorohydroxy-*compounds, which could not be resolved. 4 : 5 : 7 : 7-Tetrachloro-6-keto-2-phenyl-6 : 7-dihydro-2 : 1 : 3-benzotriazole, $\text{C}_{12}\text{H}_6\text{ON}_3\text{Cl}_4$, prepared by boiling the pentachloro-compound just described with a solution of potassium acetate in acetic acid, crystallises in slender, yellow needles, m. p. 168°, and when reduced with stannous chloride yields 4 : 5 : 7-trichloro-6-hydroxy-2-phenyl-2 : 1 : 3-benzotriazole,

$\text{C}_{12}\text{H}_6\text{ON}_3\text{Cl}_3$, slender, white needles, m. p. 167—168°, the *acetyl* derivative of which, $\text{C}_{12}\text{H}_5\text{O}_2\text{N}_3\text{Cl}_3$, crystallises in glistening, white needles, m. p. 179—180°. The trichlorophenol is oxidised by nitric acid (D 1·4) in glacial acetic acid, yielding 4 : 5-dichloro-6 : 7-diketo-2-phenyl-6 : 7-dihydro-2 : 1 : 3-benzotriazole, $\text{NPh} \begin{smallmatrix} \text{N} \cdot \text{C} \cdot \text{CO} \cdot \text{CO} \\ | \quad | \\ \text{N} \cdot \text{C} \cdot \text{CCl} \cdot \text{CCl} \end{smallmatrix}$, large, red crystals, m. p. 191°. The

latter substance undergoes the following changes : (1) When reduced, with stannous chloride, it yields 4 : 5-dichloro-6 : 7-dihydroxy-2-phenyl-2 : 1 : 3-benzotriazole, $\text{C}_{12}\text{H}_7\text{O}_2\text{N}_3\text{Cl}_2$, which crystallises in slender, white needles, sinters at about 130°, m. p. 154—155° (decomp.) when heated slowly, m. p. 170° (decomp.) when heated rapidly; the *diacetate*, $\text{C}_{12}\text{H}_5\text{O}_4\text{N}_3\text{Cl}_2$, forms glistening, slender, white needles, m. 189—190°. (2) It is converted by a hot 20% aqueous solution of sodium carbonate into 5-chloro-6-hydroxy-4 : 7-diketo-2-phenyl-4 : 7-dihydro-2 : 1 : 3-benzotriazole, $\text{C}_{12}\text{H}_5\text{O}_3\text{N}_3\text{Cl}$, large, brownish-yellow crystals, m. p. 265—266°, which, when boiled with nitric acid (D 1·4), yields the

corresponding *tetraketo-derivative*, $\text{NPh} \begin{smallmatrix} \text{N} \cdot \text{C} \cdot \text{CO} \cdot \text{CO} \\ | \quad | \\ \text{N} \cdot \text{C} \cdot \text{CO} \cdot \text{CO} \end{smallmatrix}$, crystallising in almost colourless needles, m. p. 165—170° (decomp.). (3) When treated with aniline in glacial acetic acid it yields 5-chloro-6-hydroxy-7-keto-4-phenylimino-2-phenyl-4 : 7-dihydro-2 : 1 : 3-benzotriazole,

$\text{C}_{18}\text{H}_{11}\text{O}_2\text{N}_4\text{Cl}$, which crystallises in slender, brownish-red needles with a bronzy reflex, sinters at 228°, m. p. 234—236° (decomp.).

Pentachloroketo-2-phenyltetrahydro-2 : 1 : 3-benzotriazole, when acted on by a cold 5% aqueous solution of sodium hydroxide, yields the *acid*,

$\text{NPh} \begin{smallmatrix} \text{N} \cdot \text{C} \cdot \text{CCl}_2 \cdot \text{CO}_2\text{H} \\ | \quad | \\ \text{N} \cdot \text{C} \cdot \text{CCl} \cdot \text{CHCl} \end{smallmatrix}$, which crystallises in slender, white needles,

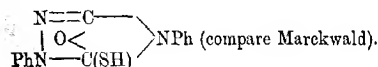
m. p. 62—63°; the *methyl ester*, $\text{C}_{13}\text{H}_5\text{O}_2\text{N}_3\text{Cl}_4$, forms slender, silky, white needles, m. p. 67—68°. An aqueous solution of the sodium salt of the acid when boiled yields the *acid*, $\text{N}_3\text{Ph} \begin{smallmatrix} \text{C} \cdot \text{CO} \cdot \text{CO}_2\text{H} \\ | \quad | \\ \text{C} \cdot \text{CCl} \cdot \text{CHCl} \end{smallmatrix}$, long, white needles, m. p. 177°, the *methyl ester* of which, $\text{C}_{13}\text{H}_5\text{O}_3\text{N}_3\text{Cl}_4$,

crystallises in glistening, white needles, m. p. 152—153°; the acid just described also results from the action of a 5% aqueous solution of sodium hydroxide on dichlorodiketophenyldihydro-2:1:3-benzotriazole.

W. H. G.

Isomeric Thiourazoles. MAX BUSCH, J. REINHARDT, and O. LIMPACH (*Ber.*, 1909, 42, 4763—4769. Compare Marckwald and Sedlacek, *Abstr.*, 1896, i, 231; Busch, *ibid.*, 1902, i, 322; Busch and Opfermann, *ibid.*, 1904, i, 630).—It is shown that the triazoles obtained from α -diarylthiosemicarbazides (Marckwald, *Abstr.*, 1899, i, 503) also exist in two isomeric forms: a labile form, for example,

1:4-diphenyl-5-thiourazole, $\text{SC} \begin{smallmatrix} \text{NPh} \cdot \text{NH} \\ \text{NPh} \cdot \text{CO} \end{smallmatrix}$, and a stable form:

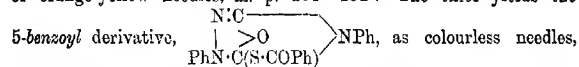


A mixture of the two compounds is formed when finely-divided α -diphenylthiosemicarbazide is suspended in benzene and shaken for two to three hours with an excess of a toluene solution of carbonyl chloride. The two urazoles are removed by shaking with 5% sodium hydroxide solution. The labile compound is precipitated on the addition of acetic acid to the alkaline liquid, and the stable compound on the addition of hydrochloric acid to the filtrate. If the mixture is shaken for a longer time, the amount of stable compound tends to increase at the expense of its isomeride. The benzene solution contains unaltered thiosemicarbazide and phenylanilinothiobiazolone (Freund and Kuh, *Abstr.*, 1890, 1440). The labile compound crystallises in colourless needles, melts at 139—140°, but is immediately transformed into the stable compound, m. p. 220°. Its *sodium* derivative crystallises in slender, felted needles, m. p. 60°, and reacts with methyl iodide at 100°, yielding diphenylmethylurazole (Busch and Heinrichs, *Abstr.*, 1901, i, 617). The *silver* salt is insoluble, and

with methyl iodide yields the *O-methyl* derivative, $\text{SC} \begin{smallmatrix} \text{NPh} \cdot \text{N} \\ \text{NPh} \cdot \text{C} \cdot \text{OMe} \end{smallmatrix}$,

m. p. 88°. When benzoylated in pyridine solution the thiourazole yields *N-benzoyldiphenylthiourazole*, $\text{C}_{21}\text{H}_{15}\text{O}_2\text{N}_3\text{S}$, as yellow needles, m. p. 146°, which are stable in the presence of alkalis.

The 5-thiol-1:4-diphenylendo-oxydihydrotriazole, when oxidised with ferric chloride, yields a *disulphide*, $(\text{C}_{14}\text{H}_{10}\text{ON}_3\text{S})_2$, in the form of orange-yellow needles, m. p. 231—232°. The thiol yields the



m. p. 189°. The *sodium* derivative of the thiol has m. p. 121°, and with methyl iodide and methyl alcohol at the ordinary temperature yields methyl mercaptan and 1:4-diphenyl-2-methylurazole.

The following diarylthiosemicarbazides also yield pairs of isomeric thiourazoles with the m. p. indicated:

2:4-Diarylthiosemicarbazide.	Thiouazole.	Thiolendo-oxy-dihydrotriazole.
4-Phenyl-2-m-tolyl	125°	259°
4-Phenyl-2-m-bromophenyl	113—119°	257
4-Phenyl-2-m-chlorophenyl	103—110	259—260
4-Phenyl-2-β-naphthyl	133—134	295
4-Phenyl-2-p-tolyl	144	233—240
4-Phenyl-2-p-bromophenyl	163—170	255

J. J. S.

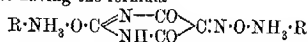
Organic Salts of Violuric Acid. TH. ZEREWITNOFF (*Ber.*, 1909, 42, 4802—4808).—Violuric acid forms intensely coloured salts with primary, secondary, and tertiary aliphatic amines and diamines, also with pyridine, piperidine, alkaloids, and some aromatic amines. The salts with primary aliphatic amines exist in two main forms, coloured blue and red (compare Hantzsch, *Abstr.*, 1909, i, 331), but usually mixtures of these are obtained resulting in violet or blue, or reddish-violet salts. Usually only one form is stable, the conversion of one into the other readily taking place in the presence of moisture. Thus *n*-propylamine, *n*-butylamine, and *n*-amylamine violurates are obtained as violet salts from alcoholic solution, but become blue on exposure to moist air, and remain blue when dried in a desiccator.

Salts of violuric acid with normal primary amines are usually red or violet in colour; those derived from primary *iso*-compounds are more often blue. The blue modification is the one generally obtained from aqueous solution.

The amine violurates are prepared by mixing the components in equimolecular proportions in alcoholic solution. The salt readily separates, and may be crystallised from alcohol or water.

Methylamine violurate is obtained violet from alcoholic solution, or blue when methyl ethyl ketone is the solvent, the violet being the stable form. *Ethylamine violurate* is at first obtained blue, but rapidly passes into the stable red form. *n*-Propylamine violurate is at first obtained blue in alcoholic solution, but the salt turns reddish-violet when left in contact with the solvent. The violet form retains its colour when dried, but changes to blue again in presence of moisture. *iso*Propylamine violurate is blue; *n*-butylamine violurate is violet, changing to blue on exposure. *iso*Butylamine violurate forms violet-blue plates or blue needles. *n*-Amylamine violurate is likewise violet, changing to blue. *iso*Amylamine violurate is at first blue, but becomes violet on recrystallisation. *tert*-Amylamine violurate is also blue; similarly, *isohexylamine violurate*, but this is violet when crystallised from water. *Heptylamine violurate* is similar.

Diamine salts having the formula



are prepared by keeping the monoamine violurate in presence of the corresponding amine in a desiccator.

Diisobutylamine violurate and *di-n*-amylamine violurate are both reddish-violet in colour.

The amine violurates dissolve in pyridine with a blue coloration. The active hydrogen atoms were determined at normal temperature

and at 85° by means of magnesium methyl iodide by the method previously described (Abstr., 1908, i, 598). The results indicate that at normal temperature only two hydrogen atoms of the NH_2 radicle are active, but at 85° all three react.

E. F. A.

Hæmopyrrole.* II. Z. LEVKO and LEON MARCHLEWSKI (*Biochem. Zeitsch.*, 1909, 22, 464—470; *Bull. Acad. Sci. Cracow*, 1909, 583—588. Compare Abstr., 1908, i, 710).—Altogether four products have been obtained by the action of benzenediazonium salts on hæmopyrrole. The main product has the formula $\text{C}_8\text{H}_{11}\text{N}(\text{N}_2\text{Ph})_2\text{HCl}$.

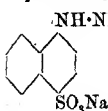
The authors now describe a method for preparing the second product, $\text{N}_2\text{Ph}\cdot\text{C}_8\text{H}_{11}\text{N}\cdot\text{C}_8\text{H}_{11}\text{N}\cdot\text{N}_2\text{Ph}\cdot\text{HCl}$, which melts at 268°. It can be separated from the chief product by means of chloroform, in which it is much more soluble, forming a bluish-violet solution, from which it can be precipitated by alcohol.

By means of sodium acetate the free base of this dye can be obtained. The authors give the measurements of the absorption bands of the chlorine-containing substance in chloroform solution. The results obtained are regarded as of importance as showing that hæmopyrrole corresponds with the formula $\text{C}_8\text{H}_{12}\text{N}$, and not $\text{C}_8\text{H}_{11}\text{N}$, and also that it is admixed with a second product corresponding with the formula $\text{C}_8\text{H}_{12}\text{N}\cdot\text{C}_8\text{H}_{12}\text{N}$, the representative of a new class of pyrrole derivatives.

S. B. S.

Action of Sulphites on Aromatic Amino- and Hydroxyl Compounds. VIII. Behaviour of Hydrazines, especially of Phenylhydrazine, in the Sulphite Reaction. HANS TH. BUCHERER and ERNST F. SONNENBURG (*J. pr. Chem.*, 1910, [ii], 81, 1—48. Compare Abstr., 1909, i, 787).—A difference has been observed in the behaviour of naphthalene derivatives of the α - and the β -series containing only one auxochromic group when these compounds undergo prolonged boiling with phenylhydrazine and 36% sodium hydrogen sulphite. The reactions are complicated by the interaction of the two last-mentioned substances to form sodium phenylhydrazinesulphonate, from which the desired reaction product cannot be separated. After decomposing the latter, however, by alkalis and by acids, the nature of the secondary products throws some light on the constitution of the primary products in the sulphite reaction. Thus amines and naphthols of the α -series (except α -naphthol itself and 1-naphthylamine-5-sulphonic acid) yield s -hydrazinesulphonates, $\text{NHR}\cdot\text{NPh}\cdot\text{SO}_3\text{Na}$ or $\text{NHPh}\cdot\text{NR}\cdot\text{SO}_3\text{Na}$, which are converted by alkali into benzenazonaphthalene derivatives, and by acid into nuclear sulphonic acids of the carbazoles, and also to some extent into diamino-compounds by the benzidine transformation. Amines and naphthols of the β -series and also the two above-mentioned exceptions of the α -series yield, after treatment with phenylhydrazine and sodium hydrogen sulphite, carbazole- N -sulphonic acids, which are probably produced from an initially-formed hydrazo-compound by intramolecular indole condensation; the absence of any hydrazo-compound among the primary products of the reaction is proved by the non-production of azo-compounds by treatment with alkali (compare Abstr., 1908, i, 455).

The reaction typical of members of the α -series is best exemplified by 1-naphthol-4-sulphonic acid, the only instance in which the initial hydrazo-compound can be separated from the sodium phenylhydrazine-sulphonate formed simultaneously. 1-Naphthol-4-sulphonic acid is boiled with phenylhydrazine and 36% sodium hydrogen sulphite for seven and a-half hours, and the white, crystalline product is extracted with boiling 95% alcohol. The alcoholic extract deposits on cooling colourless crystals, which are freed from sodium phenylhydrazine-sulphonate by treatment with benzene and with alcohol; the purified

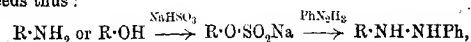


product has the composition C₁₅H₁₂O₃N₂Na₂, and is the *hydrazo*-compound, probably having the annexed constitution. By treatment with sodium hydroxide, it yields benzenazo- α -naphthalene and benzenazo- α -naphthalenesulphonic acid (each of which can be reduced to diamino-compounds), and by heating with hydrochloric acid (3:1) it is converted into α -phenonaphthacarbazole and a diamino-compound. 1-Naphthylamine-4-sulphonic acid behaves in the same way, and yields the same products, and so also does 1-naphthylamine-6-sulphonic acid, the reaction product being converted by dilute sodium hydroxide on the water-bath into benzenazo- α -naphthalene-6-sulphonic acid, and by strong hydrochloric acid into α -phenonaphthacarbazole-6-sulphonic acid

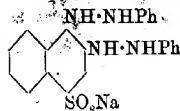
SO₃H·C₁₀H₆ < $\begin{matrix} \text{NH} \\ | \\ \text{C}_6\text{H}_4 \end{matrix}$, and a diamino-compound.

By prolonged heating with phenylhydrazine and 36% sodium hydrogen sulphite, α -naphthol yields pheno- α -naphthazole-*N*-sulphonic acid, which cannot be isolated in a solid state, but yields phenonaphthacarbazole when heated with concentrated hydrochloric acid. In a similar way, the product from 1-naphthylamine-5-sulphonic acid yields α -phenonaphthacarbazole-5-sulphonic acid (probably obtained from the *N*/5-disulphonic acid); that from 2-naphthol-1-sulphonic acid or 2-naphthylamine-1-sulphonic acid yields 2:1-phenonaphthacarbazole in small amount and 2:3-phenonaphthacarbazole-1-sulphonic acid; that from 2-naphthol-6-sulphonic acid yields phenonaphthacarbazole-6-sulphonic acid, and that from 2-naphthol-3:6-disulphonic acid yields a carbazole-3:6-disulphonic acid.

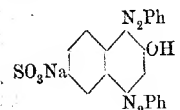
The action of phenylhydrazine and sodium hydrogen sulphite on naphthalene derivatives containing two auxochromic groups is somewhat different from that on derivatives containing only one. Carbazoles are not formed. Thus 1-amino-2-naphthol-4-sulphonic acid yields a yellow solid and a yellow solution. The solid has the composition C₂₂H₁₉O₃N₃Na, and by treatment with hot sodium hydroxide yields a bluish-red dye, from which hydrochloric acid eliminates phenylhydrazine. The yellow solution by treatment with warm concentrated sodium hydroxide yields sodium 1-benzenazo-2-naphthol-4-sulphonate, 2-benzenazo-1-naphthol-4-sulphonate, and 2-benzenazo-1-naphthol. Bearing in mind that the sulphite reaction proceeds thus:



there appears to be little doubt that the yellow solid has the annexed constitution, and that it yields the preceding azo-compounds by loss of phenylhydrazine from position 1 or 2 and simultaneous oxidation when treated with alkali. Similarly, 1-amino-2-naphthol-3:6-disulphonic acid also yields two yellow products, the one soluble, the other insoluble, which are converted by alkali into red azo dyes.

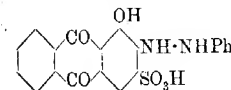


The action of phenylhydrazine and sodium hydrogen sulphite on certain azo-dyes follows a similar course. By heating 1-benzeneazo-2-naphthol-3:6-disulphonic acid with phenylhydrazine (or hydrazine hydrate) and sodium hydrogen sulphite, a yellow solid and a yellow solution are obtained, from each of which the original dye is recovered by alkali. The reaction in the case of 1-benzeneazo-2-naphthol-6-sulphonic acid is more profound. Again, a yellow solid and a yellow solution are obtained. The latter regenerates the original dye by treatment with alkali, and probably contains the hydrogen sulphite compound of the dye. The yellow solid, the analysis of which accords with the constitution $\text{SO}_3\text{Na}\cdot\text{C}_{10}\text{H}_4(\text{NH}\cdot\text{NHPh})_2(\text{NH}\cdot\text{NPh}\cdot\text{SO}_3\text{Na})$, is stable towards cold alkali, but is converted by warm dilute sodium hydroxide into a bluish-red dye, the analysis of which points to the annexed constitution.



The behaviour of a mixture of 1-benzeneazo- and 1-tolueneazo-2-naphthol-6-sulphonic acid, or of 1-xyleneazo-2-naphthol-3:6-disulphonic acid, with phenylhydrazine and sodium hydrogen sulphite is very similar to the preceding.

The behaviour of alizarin-red *S* with phenylhydrazine and sodium hydrogen sulphite has also been examined. The product is a yellowish-brown substance, which resembles the original dye in several respects but differs from it in the colour of its alkaline solution and in producing a more violet shade on chromed wool. It has probably the annexed constitution, and regenerates alizarin-red *S* and phenylhydrazine when heated with dilute hydrochloric acid.

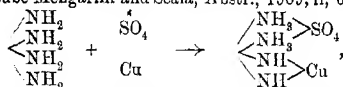


No condensation takes place when 1-naphthylamine- or 1-naphthol-4-sulphonic acid is heated with sodium hydrogen sulphite and hydrazobenzene, either together or successively; the product contains azobenzene, benzidine, and its *N*-sulphonic acid. The latter is obtained almost quantitatively when azobenzene, ammonium hydrogen sulphite, and ammonium hydroxide (D 0.88) are heated for twenty-four hours at 100–110° under 2 atmospheres pressure. C. S.

Compounds of Copper with Egg-Albumin. ALBERTO SCALA and GIUSEPPE BONAMARTINI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 551–559).—Further examination of the acid copper albumin obtained from copper sulphate and egg-albumin (compare Bonamartini and Lombardi, *Abstr.*, 1909, i, 72) shows that, after washing, this compound does not contain copper and sulphuric acid in the proportions in which they exist in copper sulphate, the copper always being

in excess. In fact, making allowance for the sulphuric acid yielded on analysis by the sulphur of the albumin, it would appear that the whole of the sulphuric acid is eliminated by washing, together with the larger part of the copper.

These observations may be explained by assuming that the copper sulphate combines with lateral amino-groups of the albumin molecule (compare Traube-Mengarini and Scala, *Abstr.*, 1909, ii, 603) thus:



giving a compound in which the degrees of dissociation and hydrolysis of the group $\begin{array}{c} \text{NH}_2 \\ \diagup \\ \text{NH}_3 \\ \diagdown \\ \text{NH}_2 \end{array} \text{SO}_4$ are greater than those of the group $\begin{array}{c} \text{NH}_2 \\ \diagup \\ \text{NH}_3 \\ \diagdown \\ \text{NH}_2 \end{array} \text{Cu}$, so that whilst the one group tends to become completely removed, the other (Cu) tends towards a limit. If, then, compounds containing at first different proportions of copper, are washed, they should yield compounds of constant type, and this is found approximately to be the case.

That this explanation is the true one is shown by the observation that, when an egg-albumin solution is treated with copper sulphate in slight excess and then with sodium hydroxide solution, a compound is obtained with a proportion of copper greater than is ever observed when no sodium hydroxide is employed; the alkali tends to detach the SO_4 groups, and at the same time introduce more Cu groups into the molecule. T. H. P.

The Scission Products of the Nucleo-protein of Milk Glands. JOHN A. MANDEL (*Biochem. Zeitsch.*, 1909, 23, 245—249).—The amino-acids and hexone bases obtained by the hydrolysis of the nucleo-protein were estimated and compared with the hydrolysis products of caseinogen. There is a decided similarity in the numbers obtained, which indicate that caseinogen is possibly a degradation product of the nucleo-protein of milk glands, and produced from the latter by a scission of carbohydrates, purine, and pyrimidine bases. Hammarsten's method was employed in the preparation of the nucleo-protein. S. B. S.

Studies on Enzymes. II. Measurement and Meaning of the Concentration of the Hydrogen Ions in Enzymatic Processes. SOREN P. L. SORENSEN (*Biochem. Zeitsch.*, 1909, 22, 352—356; *Compt. rend. Lab. Carlsberg*, 1909, 8, 1—168. Compare *Abstr.*, 1909, i, 861).—It was found that the secondary sodium phosphate employed for preparing the 1/15 mol. standard solution contained 3—4% of the primary salt. New determinations with a pure salt were accordingly made, and the results are given in a table. The new values, p_H , do not, however, differ essentially from the ones previously given except in the mixtures having the greatest alkalinity. In neutral or nearly neutral mixtures, the difference is quite small, and is sometimes positive and sometimes negative, so that the old values are retained for the whole curve. N. H. J. M.

[The Enzymes of Gum-acacia and certain other Gums.]
 VIKTOR GRAFE (*Zeitsch. Physiol. Chem.*, 1909, 63, 106-108).—A reply to some criticisms of Reinitzer (*Abstr.*, 1909, i, 751). S. B. S.

Preparation of Hydroxyarylsarsenious Oxides. FARBERWERKE VORM. MEISTER LUCIUS & BRÜNING (D.R.P. 213594).—The action of mild reducing agents, such as hydrogen iodide, sulphurous acid, phenylhydrazine, phosphorus trichloride, or thionyl chloride on hydroxyphenylarsinic acids leads to the formation of hydroxyarsenious oxides. *p*-Hydroxyphenylarsenious oxide, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}$, a colourless, crystalline powder, readily soluble in water or alcohol, is prepared by reducing sodium *p*-hydroxyphenylarsinate with potassium iodide and dilute sulphuric acid.

p-Arsenophenol, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{As}\cdot\text{As}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, is precipitated in yellow flakes when the foregoing compound is warmed in neutral solution with sodium hypochlorite. F. M. G. M.

***o*-Aminoarylsarsinic Acids.** LUDWIG BENDA (*Ber.*, 1909, 42, 3619-3622. Compare Ehrlich and Bertheim, *Abstr.*, 1907, i, 812; O. and R. Adler, 1908, i, 492; Benda and Kahn, 1908, i, 591; Bertheim, 1908, i, 590).—Arylamines with a substituent in the para-position with respect to the amino-group condense with arsenic acid, yielding *o*-aminoarylsarsinic acids, but the yields are not good. These ortho-arsanilic acids closely resemble the corresponding para-compounds in most of their properties, and can be readily acylated and diazotised. 4-Aminotolyl-5-arsinic acid, $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{AsO}(\text{OH})_2$, obtained from *p*-toluidine and arsenic acid at 195-200°, crystallises from dilute alcohol in felted needles, m. p. 176°. *m*-Xylidine and arsenic acid yield 4-amino-*m*-xylene-5-arsinic acid, $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Me}_2\cdot\text{AsO}(\text{OH})_2$, m. p. 199-200°, and *p*-chloroaniline and arsenic acid, 4-chloro-1:2-arsanilic acid, $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{AsO}(\text{OH})_2$, m. p. 207°. The position of the arsinic acid radicle can be determined by replacement by iodine. J. J. S.

Preparation of Carbamide and of Thiocarbamide Derivatives of *p*-Aminophenylarsinic Acids. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.P. 213155).—The action of cyanic or thiocyanic acids (or the corresponding esters) on *p*-aminophenylarsinic acid or its derivatives yields crystalline compounds having the general formula $\text{NRR}_1\cdot\text{CR}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}(\text{OH})_2$, where R and R_1 may be either hydrogen, aryl, or alkyl groups, and R_2 either sulphur or oxygen; these compounds are sparingly soluble in cold water or dilute mineral acids, and therapeutically less toxic than the acyl *p*-aminophenylarsinic acids. The following examples are mentioned: carbamidoarsanilic acid, thiocarbamidoarsanilic acid, phenylcarbamidoarsanilic acid, methylcarbamidoarsanilic acid, carbamido-*o*-methylarsanilic acid, and carbamidoanthranilic-arsinic acid. F. M. G. M.

Organic Chemistry.

Oxidation of Unsaturated Compounds by means of Organic Peroxides. EDUARD LIPPMANN (*Ber.*, 1910, 43, 464, Compare Prileschaeff, this vol., i, 86).—The addition of benzoyl peroxide to amylene, and the subsequent hydrolysis to isodiamylene oxide, was studied by the author in 1881 (*Abstr.*, 1885, 366).

J. J. S.

Condensation of *sec*-Butyl Alcohol with its Sodium Derivative. MARCEL GUERBET (*Compt. rend.*, 1910, 150, 183—185, Compare *Abstr.*, 1902, i, 130, 583, 657; 1908, i, 162, 635).—When *sec*-butyl alcohol is heated with its sodium derivative at 200—220° there is formed a mixture of two alcohols: (1) γ -Methylheptan- ϵ -ol, $\text{CHMeEt}\cdot\text{CH}_2\cdot\text{CHEt}\cdot\text{OH}$, a liquid with a mint-like odour, has b. p. 167—169° (corr.), D^{20} 0.8493; its acetate has b. p. 183—185° (corr.). On oxidation, the alcohol yields γ -methylheptan- ϵ -one, $\text{C}_8\text{H}_{16}\text{O}$, b. p. 161° (corr.); the semicarbazone crystallises in needles, m. p. 96°. The constitution of the foregoing alcohol and ketone was deduced from a study of their oxidation products.

(2) The dodecyl alcohol, "trise-*butylic alcohol*," $\text{C}_{12}\text{H}_{26}\text{O}$, b. p. 250—255° (corr.), an agreeably smelling liquid, is converted on oxidation into the corresponding ketone, $\text{C}_{12}\text{H}_{24}\text{O}$, b. p. 247—248° (corr.). This forms a semicarbazone, m. p. 161—162°. W. O. W.

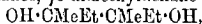
Methylacetylenylcarbinol [Butinene- γ -ol]. ROBERT LESPIEAU (*Compt. rend.*, 1910, 150, 113—114, Compare *Abstr.*, 1908, i, 496).—A description of a method for preparing alcohols of the type $\text{OH}\cdot\text{CHR}\cdot\text{C}\equiv\text{CH}$. β -Bromo- Δ^2 -butene- γ -ol, $\text{OH}\cdot\text{CHMe}\cdot\text{CBr}\cdot\text{CH}_2$, obtained by the action of magnesium methyl iodide on bromoacetaldehyde, is a colourless liquid, b. p. 59.5—60°/14 mm., or 151°/732 mm. (decomp.); it forms a phenylurethane, m. p. 62.5—63.5°. Alcoholic potassium hydroxide converts the alcohol almost quantitatively into acetylene, whilst the aqueous alkali brings about a more complex change. Amongst the products recognised were acetylene, propionic acid, and butinene- γ -ol, $\text{OH}\cdot\text{CHMe}\cdot\text{C}\equiv\text{CH}$. This was isolated, not quite free from water, as a liquid, b. p. 107—109°/760 mm. By treating with an ammoniacal cuprous chloride solution, a precipitate is formed, which, on treatment with iodine and potassium iodide, is converted into $\alpha\beta$ -tri-iodo- Δ^2 -butene- γ -ol, $\text{OH}\cdot\text{CHMe}\cdot\text{CI}\cdot\text{CI}_2$, m. p. 96°.

W. O. W.

Unsaponifiable Constituents of Japan Tallow. HERMANN MATTHIES and W. HEINTZ (*Arch. Pharm.*, 1909, 247, 650—657).—Japan tallow, m. p. 53—53.5, D 1.0032, is saponified by alcoholic potassium hydroxide, and the clear soap solution is diluted with water and extracted with ether. The residue obtained by the distillation of

the ethereal extract is submitted to a series of fractionation operations. The final residue thus obtained in 9.33% yield is a yellowish-brown mass (iodine number 36.25), which is separated by petroleum into an insoluble portion, from which myricyl alcohol is isolated, and a soluble portion, from which phytosterol, m. p. 139°, and ceryl alcohol, m. p. 79°, are obtained, together with a saturated alcohol, m. p. 65° (acetate, m. p. 41°), which is probably nonadecyl alcohol, $C_{19}H_{40}O$.
C. S.

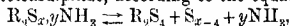
Dimethyldiethyldicarbinal $[\gamma\delta$ -Dimethylhexane- $\gamma\delta$ -diol], Mlle. Cécile FRUMINA (*Bull. Acad. roy. Belg.*, 1909, 1151—1157).—Lawrinowitsch's pinacone, obtained by reducing methyl ethyl ketone with sodium (Abstr., 1877, ii, 427), has been prepared by the action of magnesium ethyl iodide on methyl oxalate, and proved to consist of a single liquid substance, $\gamma\delta$ -dimethylhexane- $\gamma\delta$ -diol,



b. p. 195°/760 mm. or 10°/110 mm. The solid modification obtained by Zelinsky and Krapivin (Abstr., 1893, i, 390) in repeating Lawrinowitsch's experiment was not produced in the synthesis now described. The diethyl ether has b. p. 142—143°/760 mm. or 110—111°/20 mm., and is liquid. The dichloride boils at 165—166°/760 mm. or at 114—115°/18 mm.
T. A. H.

Drying of Moist Ether. E. VON SIEMENROCK (*Monatsh.*, 1909, 30, 759—766).—A comparative study of calcium chloride, potassium carbonate, sodium sulphate, magnesium sulphate, sylvite, potassium chloride, calcium sulphate, and carnallite, having regard to their use, in the anhydrous state, for the removal of water from moist ether. The first two substances mentioned are shown to be most efficacious; sodium sulphate, a substance frequently recommended and used for drying ether, is not very effective, and may be replaced with great advantage by carnallite and magnesium sulphate.
W. H. G.

Action of Sulphur and Ammonia on Organic Sulphides and Disulphides. BROR HOLMBERG. (*Ber.*, 1910, 43, 220—226. Compare Abstr., 1908, i, 308).—Organic sulphides and disulphides form reddish-brown additive products of the general formula $R_2S_x \cdot yNH_3$ with sulphur and ammonia. The reaction is reversible, the equilibrium depending on the sulphide used. In some cases, as with ethyl and *p*-tolyl disulphides, the additive product undergoes further change into the tetrasulphide, according to the equation:



so that the ammonia can be considered to act catalytically on the formation of tetrasulphides from disulphides and sulphur.

The organic sulphide or disulphide is dissolved in absolute alcohol, an excess of flowers of sulphur added, and the solution then saturated with ammonia, whereby the colour gradually changes to a dark brown. After some weeks the undissolved sulphur is collected and weighed, the filtrate allowed to evaporate spontaneously, and the residue then investigated.

With ethyl sulphide, the residue consisted of a minute trace of sulphur, but the additive product must have been formed in solution,

since the presence of ethyl sulphide is necessary for the formation of the brown colour.

Ethyl disulphide gave a residue of a yellow uncrystallisable oil; when this was distilled under diminished pressure (12 mm.), a colourless liquid distilled over at 77–78°, and the residue in the flask consisted of ethyl tetrasulphide.

p-Tolyl disulphide (prepared from *p*-tolyl mercaptan and sulphuryl chloride in ethereal solution, or by the spontaneous oxidation of an alkaline solution of the mercaptan) gave a solid residue, contaminated with oil, which after recrystallisation from alcohol is found to be a mixture of the di- and tetra-sulphide, the latter having m. p. 75°.

Diethyl dithiodiglycolate gave a dark-coloured solution, from which the original substances were always regenerated, no matter what the treatment; large quantities of sulphur dissolved. If the filtrate, after collecting the excess of sulphur, was again saturated with ammonia and kept for six weeks, the amide, m. p. 156–157°, derived from the original ester was formed.

In an appendix on the inorganic polysulphides, the author states his opinion that compounds with simple sulphur chains are colourless, or only pale yellow; a brown colour is due to the presence of larger atomic complexes, S_x . Whether the compound should be formulated as M_2S_x or M_xS_x is left undecided.

T. S. P.

Crystalline Form and Optical Characters of Lead Formate. R. KARADÉEFF (*Centr. Min.*, 1910, 17–24).—Crystals of lead formate, $Pb(CHO_2)_2$, are orthorhombic, with $a : b : c = 0.74538 : 1 : 0.84656$. Detailed determinations of the optical constants are given.

L. J. S.

[Electrolysis of Carboxy-acids.] FELIX KAUFER (*Ber.*, 1910, 43, 266).—The statement made by the author and C. Herzog (*Abstr.*, 1909, i, 870) in connexion with the attitude of Forster and Pignet (*Abstr.*, 1904, i, 965) towards the superoxide theory was incorrect. An error was also made in the reference to the work of Miller and Hofer.

R. V. S.

Formation of Dichloroacetic Acid from Trichloroacetaldehyde by Wallach's Method. ARTHUR KÖTZ (*Festschrift Otto Wallach*, 1909, 496–501. Compare Wallach, *Abstr.*, 1878, 285, 288).—The conversion of chloral into dichloroacetic acid, which may be brought about through the agency of water alone, is greatly facilitated by the presence of potassium cyanide, probably owing to the intermediate formation of chloralcyanohydrin, $CCl_3 \cdot CH(OH) \cdot CN$, and α -dichloro- β -cyano- β -hydroxyethylene, $CCl_2 \cdot C(OH) \cdot CN$, or the tautomeride, dichloropyruvitrile, $CHCl_2 \cdot CO \cdot CN$. The following observations are quoted in support of this explanation: (1) Dichloroacetic acid is formed by the action of water on chloralcyanohydrin. (2) Nitriles of dihalogenated pyruvic acids under the conditions of Wallach's method yield dihalogenated acetic acids and hydrogen cyanide. (3) Trichlorolactic acid may be converted in aqueous solution into dichloroacetaldehyde, hydrogen chloride, and carbon dioxide;

this reaction undoubtedly takes place through the intermediate formation of α -dichloro- β -hydroxyethylenecarboxylic acid or the tautomeric dichloropyruvic acid, since dihalogenated pyruvic acids decompose in aqueous solution, yielding dihalogenated aldehydes and carbon dioxide.

Chloroacetaldehyde and dichloroacetaldehyde behave similarly to chloral, with the difference that the first-named substance cannot be converted into formic acid and chloromethane.

β -Halogenated aldehydes, such as β -chloropropaldehyde, cannot be converted into the corresponding acids even under the influence of hydrogen cyanide; it would appear, therefore, that reactions of the nature under discussion only take place when halogen and oxygen are united to adjacent carbon atoms.

W. H. G.

Catalytic Phenomena. JACOB BOESEKEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 417—421).—By the researches of Perrier (*Abstr.*, 1900, i, 331) and the author (*Abstr.*, 1900, i, 349; 1901, i, 474) it has been shown that in Friedel and Crafts' reaction it is not the aromatic hydrocarbon, but the chloride or anhydride, which is first attacked by the aluminium chloride, as in many cases additive products can be isolated. The author regards this initial action as consisting of a loosening of the chloride, and possibly also of the double linkings of the benzene derivative, it being known that many reactions indicate the action of aluminium chloride to be purely a dissociating one. In order to test this view, the author has examined several additional cases, and with the idea that the reaction might proceed more readily if stable chlorine compounds, such as hydrogen chloride, could be formed during the decomposition, the substances chosen were trimethylacetyl chloride, dichloroacetyl chloride, chloral and trichloroacetyl chloride; these all contain a more or less over-loaded carbonyl group, so that the reaction could be followed by the evolution of carbon monoxide. The results obtained are as follows: Trimethylacetyl chloride is resolved at 0° according to the equation $\text{CMe}_3\cdot\text{COCl} = \text{HCl} + \text{CO} + \text{C}_3\text{H}_8$, the isobutylene being almost entirely polymerised. When gently heated, chloral undergoes decomposition in two directions: (a) $\text{CCl}_3\cdot\text{CHO} = \text{HCl} + \text{CO} + \text{CCl}_3$ (or C_2Cl_4), to the extent of 70—75%; and (b) $\text{CCl}_3\cdot\text{CHO} = \text{CO} + \text{CHCl}_3$. With dichloroacetyl chloride decomposition takes place in the two directions: $\text{CHCl}_2\cdot\text{COCl} = \text{CO} + \text{CHCl}_3$, to 60%, and $\text{CHCl}_2\cdot\text{COCl} = \text{CO} + \text{HCl} + \text{CCl}_3$, the CCl_3 presumably being polymerised to C_2Cl_4 . Trichloroacetyl chloride, when repeatedly distilled with aluminium chloride, is decomposed in one direction: $\text{CCl}_3\cdot\text{COCl} = \text{CCl}_4 + \text{CO}$.

It is remarkable that, in spite of its excess of chlorine atoms, trichloroacetyl chloride is the most difficult of attack. The reaction seems to proceed particularly smoothly in the case where hydrogen and chlorine atoms are united with two adjacent carbon atoms.

The course of the reaction with chloral and dichloroacetyl chloride indicates that it is the movable chlorine atom which is initially rendered active. The action of aluminium chloride on trimethylacetyl chloride is too violent to admit of the first stage of the reaction being ascertained. But with sulphuric acid, which in many cases

behaves analogously to aluminium chloride and forms the same kind of additive products, the reaction appearing to pass through the phases: $\text{CMe}_3\text{COCl} + \text{H}_2\text{SO}_4 = \text{CMe}_3\text{CO}\cdot\text{SO}_3\text{H} + \text{HCl}$ and $\text{CMe}_3\text{CO}\cdot\text{SO}_3\text{H} = \text{H}_2\text{SO}_4 + \text{CO} + \text{C}_4\text{H}_8$, the chlorine atom being first detached by the sulphuric acid.

T. H. P.

Detergent Action of Soap Solutions. III. WALTÈRE SPRING (*Bull. Acad. roy. Belg.*, 1909, 1059—1065; *Arch. Sci. phys. nat.*, 1910, [iv], 29, 42—48, and *Bull. Soc. chim. Belg.*, 1910, 24, 17—54.* Compare Abstr., 1909, i, 628, and this vol., i, 6).—The results obtained with "red ochre" (*loc. cit.*) have led to the extension of this investigation to the action of hydrated alumina on soap solutions. The results are analogous to those obtained with red ochre.

To each member of a series of fourteen solutions containing quantities of soap ranging from 1/2.5% to 1/16%, 2 c.c. of a mixture of water and aluminium hydroxide (equivalent to 0.0061% Al_2O_3) were added. The mixtures containing 1/8% and 1/16% of soap flocculated in twenty-four hours, and that containing 1/4% of soap flocculated in thirty-nine hours; the remaining mixtures, except that containing 1/2.5% soap, having in this time flocculated partially. Changes in the relative proportions of aluminium hydroxide and soap displace these points of flocculation, and also mask the periodicity. The coagulated product is pulverulent, like that obtained with ferric hydroxide (*loc. cit.*), and on ignition gives a mixture of about 3 mols. of alumina to 1 mol. of sodium carbonate, indicating an original adsorption product of 3 mols. of alumina with 2 of soap.

T. A. H.

Detergent Action of Soap Solutions. IV. WALTÈRE SPRING (*Bull. Acad. roy. Belg.*, 1909, 1128—1139, and *Bull. Soc. chim. Belg.*, 1910, 24, 17—54*).—Silicic acid, clay, and cellulose react with soap solutions in the same way as lampblack (Abstr., 1909, i, 628), red ochre (this vol., i, 6) and alumina (preceding abstract) forming with a part of the soap insoluble adsorption compounds, which are less adhesive than the original colloidal substances.

A soap solution in which silicic acid has been suspended, and which has been clarified by deposition, does not redden with phenolphthalein solution, and yields less alkaline ash on evaporation and ignition than the original solution, due to combination of the silicic acid with a basic portion of the soap. Such a suspension on filtration yields a filtrate containing silica, and the amount of the latter in the filtrate augments with the diminution in concentration of the soap solution (compare *loc. cit.*). Solutions of soap of strengths varying from 1/512% to 2% show periodicity in suspending power for silicic acid, the maxima being at about 1/16% and 1/2%, and the minimum at about 1/8%.

Pottery clay behaves in a similar manner. Its suspension in soap solution of any strength clears with difficulty, but a maximum suspending power is shown by a soap solution of 1/8% strength. After ignition, the clay decomposes soap less readily, and deposits much more easily from suspensions, the maximum suspending power for baked clay being shown by a soap solution of 1/32% strength.

* The last reference contains the complete paper, Parts I—IV.

Cellulose has no effect on soap in solutions containing less than 1% but for concentrations above this the soap is decomposed, a basic portion combining with the cellulose.

T. A. H.

Xanthic Acid and Dixanthogen [Ethyl Di-oxythiocarbonate].
 II. MANFRED RAGG (*Chem. Zeit.*, 1910, 34, 82—84. Compare Abstr., 1908, i, 604).—A pure xanthate can only be prepared when water is excluded from the reaction mixture in order to prevent hydrolysis. To prepare sodium xanthate, sodium is dissolved in excess of ethyl alcohol, and then the calculated quantity of carbon disulphide added, the reaction mixture being stirred and cooled meanwhile. The solution so obtained is fairly stable, and gives a yellow precipitate with copper salts which is free from the dark brown impurities which are formed when hydrolytic products are present. The yellow precipitate consists of cuprous xanthate and ethyl di-oxythiocarbonate, the reaction taking place quantitatively according to the equation: $4\text{NaS}\cdot\text{CS}\cdot\text{OEt} + 2\text{CuSO}_4 = \text{Cu}_2(\text{S}\cdot\text{CS}\cdot\text{OEt})_2 + \text{S}_2(\text{CS}\cdot\text{OEt})_2 + 2\text{Na}_2\text{SO}_4$. The dixanthogen can be extracted from the precipitate by means of carbon tetrachloride. It is noteworthy that if sodium is added to a mixture of ethyl alcohol and carbon disulphide, sodium xanthate is not formed, but a compound which gives a dark red precipitate with copper salts, and only changes into yellow cuprous xanthate on warming.

The following dixanthogens [di-oxythiocarbonates] and xanthates have been prepared in a similar manner from the corresponding alcohols:

Methyl di-oxythiocarbonate, $\text{S}_2(\text{CS}\cdot\text{OMe})_2$, is a brownish-yellow, viscid oil, with an odour different from that of the ethyl compound, and somewhat similar to that of acetone; $D = 1.180$; b. p. 123° (decomp.). *Cuprous methyl xanthate* is a pale yellow powder.

n-Propyl di-oxythiocarbonate, $\text{S}_2(\text{CS}\cdot\text{OPr})_2$.—Brown liquid with no characteristic odour; $D = 1.087$; b. p. 117° (with decomposition). *Cuprous n-propyl xanthate* forms a pale yellow powder.

isoButyl di-oxythiocarbonate, $\text{S}_2(\text{CS}\cdot\text{O}\cdot\text{C}_4\text{H}_9)_2$, is a yellow oil; $D = 1.080$; b. p. 165° . In the preparation of sodium *isobutyl xanthate*, it is necessary to use a large excess of the alcohol and to warm the reaction mixture. After the addition of the copper salt, the excess of *isobutyl alcohol* must be extracted with 40% ethyl alcohol, in which both the cuprous xanthate and the dioxithiocarbonate are insoluble. *Cuprous isobutyl xanthate* is a light yellow powder.

Amyl di-oxythiocarbonate, $\text{S}_2(\text{CS}\cdot\text{O}\cdot\text{C}_5\text{H}_{11})_2$, was prepared from ordinary commercial amyl alcohol. Dark yellow oil; $D = 1.007$; b. p. 158° . *Cuprous amyl xanthate* is pale yellow in colour.

Benzyl di-oxythiocarbonate, $\text{S}_2(\text{CS}\cdot\text{O}\cdot\text{C}_6\text{H}_5)_2$.—Yellow oil with a characteristic, but not unpleasant odour; $D = 1.218$. *Cuprous benzyl xanthate* is coloured pale yellow, and is stable up to 60° . *Sodium benzyl xanthate* can be recrystallised from alcohol, but the aqueous solution gradually decomposes.

Attempts to prepare glycerol derivatives were unsuccessful, although the results obtained point to the existence of a cuprous glyceryl monoxanthate.

T. S. F.

Addition of Acid Anhydrides to Aldehydes and Ketones.
 RUMBLE, W. S. GARDNER, and ERNST SEITZ (*Monatsh.*, 1909, 30, 825-869).—Acid anhydrides, for example, the anhydrides of acetic acid, propionic acid, chloroacetic acid, and benzoic acid, react with aldehydes in the presence of sulphuric acid, yielding di-esters of the aldehyde hydrates; of all the aldehydes investigated, citronellal alone did not behave in this manner, owing to the extreme readiness with which it is decomposed by acids. In the absence of sulphuric acid and at high temperatures, esters of the enolic form of the aldehyde are chiefly formed (compare Semmler, Abstr., 1909, i, 364). The mode of action of the sulphuric acid is not clear; that the mixed anhydride which is possibly formed is directly concerned in the esterification of the aldehyde is not probable, for the sulphuric acid may be replaced by hydrochloric acid, in which case the mixed anhydride is acetyl chloride, but acetyl chloride reacts with aldehydes, yielding acetates of chlorinated alcohols and only very small quantities of aldehyde diacetates. The sulphuric acid may likewise be replaced by nitric acid, phosphoric acid, or oxalic acid, but not by 3-nitrophthalic acid, although this is a stronger acid than oxalic acid; possibly the acid, in this case, is converted into the anhydride, and is thus replaced by acetic acid.

Attempts to acetylate acetone, acetophenone, and benzophenone have proved unsuccessful.

The aldehyde diacetates are hydrolysed quite readily by hot water, and are decomposed by phenylhydrazine, with the formation of aldehyde phenylhydrazones and $\alpha\beta$ -acetylphenylhydrazine. The di-benzoates are hydrolysed by hot, but not by cold, aqueous potassium hydroxide.

Certain of the compounds mentioned later are extremely poisonous.

The following compounds, all of which have been prepared by various investigators in different ways, are readily obtained by the interaction of the aldehyde and acid anhydride under the influence of sulphuric acid: methylene diacetate, ethylidene diacetate, heptylidene diacetate, chloral diacetate, crotonaldehyde diacetate, cinnamylidene diacetate, ethylidene dipropionate, chloral bischloroacetate, b. p. 168°/10 mm. (compare Gabutti, Abstr., 1900, i, 370), and methylene dibenzoate. The interaction of salicylaldehyde and acetic anhydride in the presence of sulphuric acid leads to the formation of *o*-acetyloxyl benzaldehyde diacetate; salicylaldehyde diacetate is not formed, as stated by Perkin (*Annalen*, 1868, 146, 371), neither could it be obtained in the manner described by Barbier (Abstr., 1880, 463).

Propylidene diacetate, $C_7H_{12}O_4$, is a colourless liquid, b. p. 184–185° (corr.); *isobutylidene diacetate*, $C_8H_{14}O_4$, is a liquid with a not unpleasant odour, b. p. 189° (corr.); *benzylidene dipropionate*, $C_{12}H_{16}O_4$, is an oil, b. p. 158–159°/10 mm.; *chloral dibenzoate*, $C_{10}H_{10}O_4Cl_2$, forms large, well-defined, glistening crystals, m. p. 63–65°; *benzylidene dibenzoate*, $C_{21}H_{18}O_4$, crystallises in long, silky needles, m. p. 61–62°; *o*-nitrobenzylidene dibenzoate, $C_{21}H_{15}O_4N$, is dimorphous, m. p. 123–124° and 147–148°; it decomposes when distilled in a vacuum, yielding *o*-nitrobenzaldehyde and benzoic acid; *m*-nitrobenzylidene dibenzoate forms rosettes of silky, white crystals, m. p.

97—99°; the *para*-isomeride has m. p. 118°; *cinnamylidene dibenzoate*, $C_{25}H_{18}O_4$, crystallises in needles, m. p. 133—135°.

Ethylidene dibenzoate, $C_{16}H_{14}O_4$, could not be prepared by the sulphuric acid method; it is obtained by the action of benzoic anhydride on ethylidene diacetate in the presence of a small quantity of sulphuric acid at 100°, and forms small, glistening crystals, m. p. 70—71°.

W. H. G.

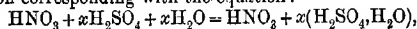
Vicianose, a New Reducing Sugar Containing C_{11} . GABRIEL BERTRAND and GUSTAVE WEISWEILLER (*Compt. rend.*, 1910, 150, 180—182. Compare Abstr., 1906, i, 68; 1908, i, 817).—The cyanogenetic glucoside observed by Bruyning (Abstr., 1900, ii, 160) in the seeds of *Vicia angustifolia* undergoes hydrolysis when treated with a diastase occurring in the seeds. A new sugar, *vicianose*, $C_{11}H_{20}O_{10}$, has been isolated from the products of hydrolysis. This is the first biose isolated from a glucoside. The compound crystallises in spherular aggregates of small needles; it is very soluble in water, but only sparingly so in alcohol. A 10% aqueous solution, after fifteen minutes, shows $\alpha_D^{20-22} + 15.8^\circ$ (300 mm. tube), but after twenty-two hours the rotation remains constant at $\alpha_D^{20} + 9.32^\circ = [\alpha]_D + 39.72^\circ$. Vicianose has m. p. about 210°; it has a somewhat higher cupric reducing power than maltose, and is not fermented by yeast.

W. O. W.

Theory of the Nitration of Cellulose. ALEXIS V. SAPOSCHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1712—1741. Compare Abstr., 1907, i, 390).—The author first discusses the work of previous investigators on the action of nitric acids of various concentrations, either alone or mixed with sulphuric acid, on cellulose.

The non-homogeneity of nitro cellulose is due largely to the dilution of the nitrating mixture by the water developed in the reaction, the external parts of the mass being more highly nitrated than the inner parts. The final degree of nitration is influenced by the reversibility of the process. If the nitric acid employed is sufficiently concentrated to form nitric ethers of cellulose, and if it is in sufficiently great excess, chemical action proceeds very rapidly. Thus, with a mixture containing 23.8% HNO_3 , 71.5% H_2SO_4 , and 4.7% water at 20°, it was found that, after two minutes, only 1.8% of the cellulose (cotton) remained unattacked, the nitrated part containing 12.7% of nitrogen, corresponding with the introduction of $10NO_2$; after five minutes, $11NO_2$ were introduced. These results, together with those obtained with a nitrating mixture composed of 30% HNO_3 , 65% H_2SO_4 , and 5% H_2O , are in accord with those obtained by Lunge and Bebie (Abstr., 1901, i, 508).

Ternary mixtures of sulphuric and nitric acids and water were investigated by determining the densities, electrical conductivities, and partial pressures of the vapours of nitric acid in the mixtures (compare Abstr., 1904, ii, 251, 558, 614; 1905, ii, 583). The results obtained indicate that in such mixtures there occurs a reversible process of the type: $HNO_3 \cdot xH_2O + H_2SO_4 \rightleftharpoons HNO_3 \cdot (n-x)H_2O + H_2SO_4 \cdot xH_2O$. This dehydration of nitric acid reaches a limit with a mixture of the composition corresponding with the equation:



further addition of sulphuric acid resulting in the formation of nitric anhydride. The results of the investigation of these ternary mixtures are given in the form of a triangular diagram (compare Abstr., 1907, i, 390).

The relation between the composition of the nitrating mixture and the degree of nitration of cellulose is discussed with the help of a large number of numerical results.
T. H. P.

Synthesis of the Phospho-organic Acid of the Seeds of Plants (Posternak's Anhydroxymethylene-diphosphoric Acid). ANGELO CONTARDI (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 23—27).—By the interaction of inosite and phosphoric acid in a current of carbon dioxide, the author has prepared an acid, $C_6H_{18}O_{24}P_6$, which exhibits all the physical and chemical characters of the phospho-organic acid obtained from the seeds of plants (compare Abstr., 1909, i, 203). By treating its barium or calcium salt with cupric and sodium acetates, the salt $C_6H_6O_{24}Cu_4Ba_2$ or $C_6H_6O_{24}Cu_4Ca_2$ is obtained, whilst the calcio-magnesium salt agrees in chemical and physical properties with the corresponding derivative of the phytin extracted from rice bran (*loc. cit.*). On hydrolysis, the acid yields compounds poorer in phosphorus, one of which, *inosite-diphosphoric acid*, $C_6H_{14}O_{12}P_2$, was isolated as a white, deliquescent, vitreous mass, and its barium salt, $C_6H_{10}O_{12}P_2Ba_2$, prepared and analysed.
T. H. P.

Phosphoric Acid Esters of Carbohydrates. I. On Sucrose-phosphoric Acid. CARL NEUBERG and H. POLLAK (*Biochem. Zeitsch.*, 1910, 23, 515—517).—Sucrose in water, freshly prepared calcium oxide, phosphoryl chloride, and dry chloroform were kept together at the temperature of melting ice, and the following reaction took place:

$$2C_{12}H_{22}O_{11} + 2POCl_3 + 5CaO = 3CaCl_2 + H_2O + 2C_{12}H_{12}O_{10} \cdot O \cdot PO_2Ca.$$

The sucrose-phosphate of calcium was separated out and analysed; it is a fine, white powder, readily soluble in water. The entrance of phosphoric acid into the sucrose molecule completely abolishes its fermentability.
W. D. H.

Lipoproteins and the meaning of Fatty Degeneration in Cells. V. Further Syntheses of Lipopeptides. VI. Further Researches on the Cleavage of Lipopeptides. S. BONDI and FRANZ EISSLER (*Biochem. Zeitsch.*, 1910, 23, 499—509, 510—513. Compare Abstr., 1909, i, 458, 459).—In continuation of former work, and by the use of the same methods, the following were prepared: Butyrylglycine, m. p. 70°. Butyrylalanine, thin prisms, m. p. 88—93°; its *ethyl* ester has b. p. 135—145°/14 mm. Butyrylalanylglycine, thin prisms, m. p. 171°. Palmitylalanylglycine, needles, m. p. 128—138°, not sharp. Laurylalanylglycine, groups of needles, m. p. 141°. *iso*-Valerylalanylglycine, thin prisms, m. p. 87—90. Laurylpeptone, crystalline. Palmitylpeptone, a brownish-yellow powder. Witte's peptone was used in the preparation of the two last-named substances. Unlike proteins and nearly all non-aromatic amino-acids, they are all readily soluble in alcohol. They are insoluble in light petroleum, and almost so in ether.

Butyrylamine is not resolved by *Phenylalanine* and is by an extract of autolysed kidney; butyrylamine is only slightly decomposed by a similar extract of liver. Trypsin has also no action on butyrylalanine or laurylalanine. The latter substance, however, is decomposed by autolysed kidney extract. No evidence of reversible action was found.

W. D. H.

A New Method of Forming *iso*Cyanates [Carbimides] and Hofmann's Thiocarbimide Reaction. II. RICHARD ANSCHÜTZ (*Annalen*, 1910, 371, 201—226. Compare Abstr., 1908, i, 326).—The behaviour of the mercuric and chloromercuric salts of ethylthiolcarbamic acid and isobutylthiolcarbamic acid when heated alone, likewise the decomposition of mercuric and chloromercuric ethyldithiocarbamates by boiling water and by heat alone, has been investigated quantitatively, with the result that the conclusions published previously (*loc. cit.*) have to be modified slightly.

Chloromercuric ethylthiocarbamate when heated decomposes thus: $3\text{NHEt}\cdot\text{CO}\cdot\text{SHgCl} \rightarrow \text{Hg}_3\text{S}_2\text{Cl}_2 + \text{COS} + 2\text{EtNCO} + \text{NH}_4\text{EtCl}$; in this way it is possible to prepare alkylcarbimides without difficulty. The corresponding ethyldithiocarbamate is decomposed by heat analogously.

Mercuric ethylthiocarbamate when heated alone decomposes into red mercuric sulphide, carbonyl sulphide, and *s*-diethylcarbamide; the formation of hydrogen sulphide could not be detected, owing to the readiness with which it interacts with ethylcarbimide, yielding carbonyl sulphide and *s*-diethylcarbamide. Mercuric ethyldithiocarbamate, when similarly treated, decomposes in two ways, represented by the equations: $[\text{NHEt}\cdot\text{CS}\cdot\text{S}]_2\text{Hg} \rightarrow (1) \text{HgS} + \text{CS}_2 + \text{CS}(\text{NHEt})_2$, or $(2) \text{HgS} + \text{H}_2\text{S} + 2\text{EtNCS}$; the mercuric sulphide obtained in these reactions is black. The extent to which the reaction represented by (2) takes place depends on the rate of heating, for hydrogen sulphide and ethylthiocarbimide interact, yielding carbon disulphide and *s*-diethylcarbamide. The salt undergoes the same change when boiled with water, but to a greater extent (about 50%) in the manner indicated by (2). In the preparation of alkylcarbimides by Hofmann's method, however, an excess of mercuric chloride is employed; this results in the formation of chloromercuric ethyldithiocarbamate, which is decomposed by boiling water, thus: $\text{NHEt}\cdot\text{CS}\cdot\text{SHgCl} = \text{HgS} + \text{SCN}\cdot\text{Et} + \text{HCl}$.

The isobutyl salts undergo the same changes as the analogous ethyl compounds.

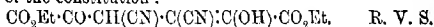
Chloromercuric ethyldithiocarbamate is prepared by adding an aqueous solution of ethylammonium ethyldithiocarbamate to a cold solution of mercuric chloride in acetone; it crystallises in white leaflets.

W. H. G.

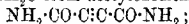
Ethyl Oxalosuccinonitrile and Diethyl Dioxalosuccinonitrile. WILHELM WISLIGENUS and HEINRICH ELYERT (*Ber.*, 1910, 43, 228—234. Compare Abstr., 1908, i, 965).—Ethyl oxalosuccinonitrile has m. p. 112—113°, not 102—103° as previously stated. A better yield is obtained if the method of preparation formerly given is modified

so as to avoid the presence of an excess of succinonitrile throughout the reaction. According to observations made by A. Hantzsch and H. Ley, alcoholic solutions of the β -form fluoresce. H. Ley and von Engelhardt find that 0.005*N*-alcoholic solutions of the α -form also fluoresce, but the fluorescence disappears when an excess of sodium ethoxide is added, so that it is due to the presence of a small proportion of the β -form.

By doubling the quantities of ethyl oxalate and potassium ethoxide taken, and reversing the order of addition in the method formerly described for the preparation of ethyl oxalosuccinonitrile, the dipotassium salt of diethyl dioxalosuccinonitrile may be obtained (compare Michael, Abstr., 1903, i, 736). The substance gives a deep reddish-brown coloration with ferric chloride, and ammonia is evolved when it is boiled with ammonium chloride. On acidifying its aqueous solution, the monopotassium salt is precipitated. It forms small, lustrous needles, m. p. above 140° (decomp.), and gives a red coloration with ferric chloride. Copper acetate yields with both potassium salts and with the free nitrile the same monocopper salt, in the form of small green needles, which become brown at 170° , and melt at $230-225^\circ$. By acidifying an aqueous solution of the potassium salt, the enolic form of diethyl dioxalosuccinonitrile may be obtained as a viscous, brown oil, which, on shaking with water, yields a hydrate which forms colourless needles, m. p. $52-53^\circ$, gives a weak red coloration with ferric chloride, and is probably the dihydrate. It readily loses water, forming the monohydrate, m. p. $102-104^\circ$. This hydrate also gives a weak red coloration with ferric chloride. The enolic form and its hydrates change spontaneously into the ketonic form, which crystallises in yellow prisms, m. p. $123-124^\circ$ (Michael, *loc. cit.*). The alcoholic solutions of this substance do not fluoresce. It is probably a ketonic enol of the constitution:



Carbon Subnitride, C_4N_2 . CHARLES MOUREU and J. CH. BONGRAND (*Compt. rend.*, 1910, 150, 225-227).—This substance has been obtained by the elimination of $2\text{H}_2\text{O}$ from acetylenedicarboxylamide,



it may therefore be regarded as dicyanoacetylene, $\text{NC}\cdot\text{C}\equiv\text{C}\cdot\text{CN}$. The analysis of the compound presented difficulties, but it has been shown to contain less than 0.6% of hydrogen. Carbon subnitride occurs as slender, colourless needles, m. p. $20.5-21^\circ$, b. p. $76^\circ/753 \text{ mm.}$, $D_4^{20} 0.9703$. The vapour is powerfully irritant, and has an odour resembling that of cyanogen; at 130° it is spontaneously inflammable in air, burning with a flame like that of cyanogen. The molecular refractions for the *D*-sodium line and for the α , β , and γ -hydrogen lines have been determined: M_D , 21.641; $M_\gamma - M_\alpha$, 1.023. Refraction and dispersion are considerably higher than the values calculated on the assumption that the compound has the foregoing constitution (compare Abstr., 1906, ii, 1), probably through the contiguity of the three triple linkings.

The vapour density between 56° and 184° is in agreement with the formula C_4N_2 . W. O. W.

Naphthene Formation. IV. Formation of Naphthene from Olefines and from Artificial Lubricating Oil and the Synthesis of the Latter. CARL ENGLER and O. ROUTALA (*Ber.*, 1910, 43, 388—397).—The conversion of olefines into naphthenes does not, as a rule, take place directly. Probably, in the first place, polymerisation to polyolefines takes place, and these, on account of their content of labile hydrogen atoms, yield, firstly, paraffins, and subsequently decompose into naphthenes, on the one hand, and lubricating oils, on the other.

When the decomposition is carried out at low temperatures, for example, with aluminium chloride at the ordinary temperature, or at the boiling point of amylene, relatively little naphthene is formed along with paraffins and lubricating oil; at higher temperatures relatively more naphthene is formed, and the lubricating oils in part decompose, forming naphthene.

When amylene is heated in tubes under pressure, methane and hydrogen are formed. By the action of aluminium chloride on amylene in the cold, an oil is formed containing more than 87% of carbon, having the composition C_nH_{2n-6} , and agreeing in composition and properties with natural lubricating oil.

When heated for some time at 350°, the lubricating oil gives rise to a mixture of unsaturated and saturated hydrocarbons; the lower boiling fractions are in the main homologues of methane, the higher boiling fractions contain increasing proportions of naphthenes.

E. F. A.

Naphthene Formation. V. The Products of Heating Cylinder Oil Under Pressure. CARL ENGLER and B. HALMAI (*Ber.*, 1910, 43, 397—405).—Large quantities of a Baku cylinder oil were heated from four to six hours under pressure at 400—430°. The product (b. p. 25—250°) was carefully fractionated, and the constituents of the successive fractions identified. The earlier fractions contained almost entirely paraffin hydrocarbons; as the boiling point rose, the proportion of naphthenes present increased. The highest boiling fractions consisted of lubricating oils, which behaved in a similar manner to the natural oils and those synthesised from amylene.

E. F. A.

Naphthene Formation. VI. Possible Formation of Hydrocarbons in Nature, and the Origin of the Optical Activity of Petroleum. CARL ENGLER (*Ber.*, 1910, 43, 405—411. Compare preceding abstracts).—In nature, bituminated animal and plant residues break down into solid paraffins, olefines, and liquid paraffins. The effect of heat and pressure, in conjunction with long periods of time, causes the solid paraffins to break down into liquid paraffins and olefines. The olefines condense to polyolefines; this gives rise to liquid paraffins, naphthenes, and lubricating oils; the last at a still higher temperature undergo further decomposition into liquid paraffins, naphthenes, and lubricating oils with less hydrogen. None of these changes is reversible. They take place simultaneously, and no great heat is required if the period of time be long enough. The petroleum

which have been exposed to the highest temperature contain most naphthenes and lubricating oils, although they may be younger in the geological sense than oils which contain mostly paraffins and have been exposed to lower temperatures.

The explanation given is in agreement with the fact that oils rich in naphthenes are usually rich in lubricating oils and vice versa. The higher boiling fractions of the heated natural cylinder oil (see previous abstract) still preserve some optical activity, and it would appear that the optically active constituents of petroleum oppose great resistance to racemisation by heat. Inasmuch as the heat in the natural process is probably less than that used experimentally, the fact that the natural petroleum is optically active is not in opposition to the combined heat and pressure theory of their formation. E. F. A.

Relation between Colour and Constitution. IWAN OSTROMISLENSKY (*Ber.*, 1910, 43, 197—198).—A claim for priority. Werner's observations on nitro-compounds and his deductions therefrom (this vol., i, 20) had been made by the author in a paper sent to, but not published by, the German Chemical Society. C. S.

Hydrocarbons from Cinnamyl Chloride, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\text{Cl}$. HANS RUPE and J. BERGIN (*Ber.*, 1910, 43, 172—178).—Cinnamyl chloride, prepared by the action of hydrogen chloride gas on cinnamyl alcohol (compare Emde, *Abstr.*, 1909, i, 708), is a mobile liquid, b. p. 116—117°/12 mm., solidifying to large, colourless needles, m. p. 8—9°. Cinnamyl bromide is obtained on heating cinnamyl alcohol with phosphorus tribromide in benzene solution in colourless needles, m. p. 30°, b. p. 130°/10 mm.

Cinnamyl chloride reacts with magnesium in ethereal solution; the product when decomposed with water yields a mixture of two hydrocarbons.

$\alpha\zeta$ -Diphenyl- $\Delta^{\alpha\alpha}$ -hexadiene, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CHPh}$, forms thin, irregular, colourless, lustrous plates, m. p. 82°, b. p. 211°/11 mm., which in solution show a reddish-blue fluorescence. It yields a tetra-bromide, separating in colourless, feathery needles, m. p. 194°.

$\alpha\delta$ -Diphenyl- Δ^{α} -hexene, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CHPh}$, is a colourless, mobile fluid, b. p. 190°/11 mm., D^{20}_D 0.9915, n^{20}_D 1.588; the hydro-bromide is a dark viscid oil. The constitution is indicated by the fact that, on oxidation with potassium permanganate, benzoic acid and phenylsuccinic acid are formed.

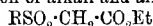
γ -Chloro- α -phenylpropane could not be prepared. γ -Bromo- α -phenylpropane is obtained by the action of phosphorus tribromide on hydrocinnamyl alcohol; the colourless liquid has b. p. 109°/11 mm. The bromide interacts with magnesium, forming propylbenzene and diphenylhexane. E. F. A.

Mobility of the Hydrogen Atoms of the Methylene Group in Compounds of the General Formulæ

$\text{R}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CN}$, $\text{R}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, $\text{R}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$.

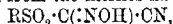
JULIUS TRÖGER and E. LUX (*Arch. Pharm.*, 1909, 247, 618—649).—The

close analogy between β -sulphoneacetic acids and β -ketonic acids, studied by Rössing (Abstr., 1890, 781) and Engelhardt (*J. pr. Chem.*, 1889, [ii], 40, 540) and further illustrated by Michael and Comay by the preparation of the sodium and alkyl derivatives of the former (Abstr., 1884, 319; 1885, 906; 1890, 781), suggests that the groups RSO_2 and CO_2Et exert the same influence as the groups RCO and CO_2Et on the neighbouring methylene group. The mobility of the methylene hydrogen atoms in arylsulphoneacetonitriles has already been shown to some extent by Tröger and Hille (Abstr., 1905, i, 336), whilst the similar behaviour of such nitriles and phenylacetonitrile with amyl nitrite and sodium ethoxide and with aldehydes and sodium hydroxide has been manifested by Tröger and Prochnow (Abstr., 1908, i, 798). The present paper deals with the influence on the methylene hydrogen atoms of compounds $\text{RSO}_2\cdot\text{CH}_2\cdot\text{X}$ exerted by different groups X (where $\text{X} = \text{CO}_2\text{R}$, $\text{CO}\cdot\text{NH}_2$, or CN), the case of arylsulphonated acetamides being of special interest, since Tröger and Lindner (Abstr., 1908, i, 633) have shown that the methylene hydrogen atoms of the corresponding arylsulphonated thioacetamides are not replaceable by alkali metals or alkyl groups. The results of experiments on arylsulphonated acetoneitriles, amides, and esters with alkalis, alkyl halides, aldehydes, and amyl nitrite and sodium ethoxide show that in these compounds the group $\text{CO}\cdot\text{NH}_2$ does not act like CN , and exerts an influence similar to, but weaker than, that of the group CO_2Et . For example, with alkalis, arylsulphonated acetic acids yield carbon dioxide and sulphones; their esters yield disodium derivatives; arylsulphonated acetamides are insoluble in sodium hydroxide, and arylsulphonated acetoneitriles, although soluble in dilute sodium hydroxide, are not hydrolysed even by boiling, this only being effected by concentrated hydrochloric acid under pressure. The action of alkali and alkyl halides on



leads, as is known, to the formation of mono- and di-alkyl derivatives, on $\text{RSO}_2\cdot\text{CH}_2\cdot\text{CN}$ only to the production of dialkyl derivatives, and on $\text{RSO}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ results in simple hydrolysis by the alkali.

Amyl nitrite and sodium ethoxide simply hydrolyse arylsulphonated acetic esters, but react smoothly with the amides and nitriles to form oxinitroso-compounds by replacement of the methylene hydrogen atoms. The compounds obtained from the nitriles have the formula



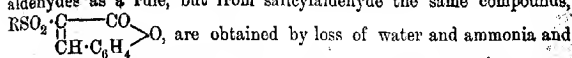
and the following oximes and their derivatives are described; the sodium and silver salts are yellow powders, and the lead salts yellowish-white powders.

R.	m. p.	Methyl ether, m. p.	Benzyl ether, m. p.	Benzoyl derivatives, m. p.	Acetyl derivatives, m. p.
Ph	—	37°	75°	153°	91°
<i>p</i> -C ₆ H ₄ Me	—	89	90	—	—
<i>p</i> -C ₆ H ₄ Cl	147°	115	80	162	126
<i>p</i> -C ₆ H ₄ Br	—	125	98	171	149
<i>p</i> -C ₆ H ₄ I	171	125	129	175	166
OMe·C ₆ H ₄	152	94	102	—	—
OEt·C ₆ H ₄	147	87	97	—	—

The following compounds, $\text{RSO}_2\cdot\text{C}(\text{NOH})\cdot\text{CO}\cdot\text{NH}_2$, are obtained in

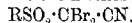
a similar salt, but less readily from arylsulphonated acetamides; the figures are: $R = Ph$, 153° (decomp.); $R = p-C_6H_4Cl$, 155° (decomp.); $R = p-C_6H_4Br$, 152° (decomp.); $R = p-C_6H_4I$, 176° (decomp.). The sodium, silver, and lead salts have been prepared.

Trigg and Prochnow (*loc. cit.*) have shown that arylsulphonated acetonitriles, like phenylacetonitrile, readily condense with certain aromatic aldehydes in the presence of a little sodium hydroxide. Arylsulphonated acetamides or acetic esters do not condense with aldehydes as a rule, but from salicylaldehyde the same compounds,



are obtained by loss of water and ammonia and water and ethyl alcohol respectively. Of such compounds, the following are mentioned: $R = Ph$, 219° ; $R = p-C_6H_4Cl$, 243° ; $R = p-C_6H_4Br$, 244° ; $R = p-C_6H_4I$, 248° .

The bromination of arylsulphonated acetic acids, esters, and amides does not proceed smoothly, but the nitriles yield compounds,



which are also obtained by the action of bromine on the sodium salts of the corresponding oximes: $R = Ph$, 123° ; $R = p-C_6H_4Cl$, 126° ; $R = p-C_6H_4Br$, 129° ; $R = p-C_6H_4I$, 131° . C. S.

Aniline Antimonyl Tartrate. PAUL YVON (*Compt. rend.*, 1910, 150, 283—285).—Clarke's salt, $C_4H_5O_6(SbO) \cdot C_6H_5N$ (Abstr., 1882, 1051), separates with 1 mol. H_2O when allowed to crystallise from an aqueous solution at 15° ; the crystals deposited at 35° are anhydrous. The hydrated salt forms stellate clusters of long prisms, which become opaque on exposure, losing water of crystallisation.

In 2—5% aqueous solution, the anhydrous salt has $[\alpha]_D^{20}$ 121.28°, D^{18} 2.112; one gram of the substance is soluble in 6.36 grams of water at 15° . The hydrate has $[\alpha]_D^{20}$ 115.61°, D^{20} 1.569.

The solubilities in water and alcohol at different temperatures are given, and also crystallographic details of the anhydrous salt.

W. O. W.

Complex Compounds of Aluminium Bromide with Organic Compounds. IWAN A. KABLUKOFF and AL. SACHANOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1755—1762. Compare Menshutkin, Abstr., 1909, i, 897, 900).—Investigation of the melting-point curves of mixtures of aluminium bromide with benzene, toluene, xylene, naphthalene, dibromomethane, bromobenzene, and *p*-dibromobenzene indicates either a slight tendency of these organic compounds to give double compounds with aluminium bromide, or the extreme instability of such complex compounds. It seems, indeed, that for stable compounds to be formed with aluminium bromide, the presence of oxygen or nitrogen in the organic component is a necessary condition.

With aniline, four compounds are formed by aluminium bromide: $Al_2Br_6 \cdot 2NH_2Ph$, m. p. 90° ; $Al_2Br_6 \cdot 3NH_2Ph$, m. p. 114° ;

$Al_2Br_6 \cdot 4NH_2Ph$, m. p. 105° ; $Al_2Br_6 \cdot 5NH_2Ph$, m. p. 122° . These compounds dissolve in benzene or ether, and are decomposed by water, giving aluminium hydroxide and aniline hydrobromide.

p-Bromoaniline gives two compounds: $\text{Al}_2\text{Br}_6 \cdot 2\text{C}_6\text{H}_4\text{Br} \cdot \text{NH}_2$, m. p. 140°, and $\text{Al}_2\text{Br}_6 \cdot 5\text{C}_6\text{H}_4\text{Br} \cdot \text{NH}_2$, m. p. 125°. Diphenylamine gives the compound $\text{Al}_2\text{Br}_6 \cdot 2\text{NHPh}_2$, m. p. somewhat above 200°; dimethylaniline, $\text{Al}_2\text{Br}_6 \cdot 2\text{NMe}_2\text{Ph}$, m. p. 95°; methylaniline,

$\text{Al}_2\text{Br}_6 \cdot 2\text{NHMePh}$, m. p. 78°; nitrobenzene, $\text{Al}_2\text{Br}_6 \cdot 2\text{Ph} \cdot \text{NO}_2$, m. p. 84°; pyridine, $\text{Al}_2\text{Br}_6 \cdot 4\text{C}_5\text{NH}_5$, m. p. about 170° (decomp.); benzonitrile, the three compounds: $\text{Al}_2\text{Br}_6 \cdot 2\text{Ph} \cdot \text{CN}$, m. p. 140–150°; $\text{Al}_2\text{Br}_6 \cdot 3\text{Ph} \cdot \text{CN}$, m. p. about 140°, and $\text{Al}_2\text{Br}_6 \cdot 4\text{Ph} \cdot \text{CN}$, m. p. about 150°.

Of the oxygenated compounds, acids, alcohols, aldehydes, and ketones form double compounds with aluminium bromide (compare Walker and Spencer, *Trans.*, 1904, 85, 1106). Further, esters of benzoic acid give compounds of the formula $\text{Al}_2\text{Br}_6 \cdot 2\text{Ph} \cdot \text{CO}_2\text{R}$, that formed by methyl benzoate having m. p. 100°. Esters of fatty acids react energetically with aluminium bromide, hydrogen bromide being evolved.

The double compounds formed by aluminium bromide with organic nitrogen compounds are more stable than those containing organic oxygen compounds. The existence of complex compounds containing an odd number of molecules of an organic compound leads to the conclusion that the aluminium bromide present exists in the form of a doubled molecule, Al_2Br_6 .
T. H. P.

Preparation of Sodium Arylimides. DEUTSCHE GOLD- & SILBER-SCHNEIDE-ANSTALT (D.R.-P. 215339).—The replacement of an aminic hydrogen atom by sodium in aniline has been shown to occur only after prolonged heating at a high temperature.

It is now found that the reaction takes place much more readily in the presence of a catalytic agent, such as copper, nickel, cobalt, or any other heavy metal, its oxide, or salt.

Under these conditions, sodium reacts with aniline at 140°; the reaction also takes place with *o*-toluidine or methylaniline; the products are hygroscopic, fairly-stable substances, but are decomposed by water into sodium hydroxide and original base. F. M. G. M.

Preparation of Cerium Phenoxides. CHEMISCHE FABRIK AUF AKTIEN FORM. E. SCHERING (D.R.-P. 214782).—The compounds formed by the interaction of cerium salts with phenolic compounds have similar disinfectant properties to the bismuth phenoxides, but are less toxic and irritating than the phenols themselves.

Cerium phenoxide, prepared from cerium nitrate, phenol, and sodium hydroxide, is pale brown, odourless, and insoluble in water; it contains 31% cerium.

Cerium o-methoxyphenoxide analogously prepared is pink, insoluble in water, but soluble in alcohol, chloroform, or ether.

Cerium β-naphthoxide has similar properties, and contains 30% of cerium. F. M. G. M.

Behaviour of Phenyl Sulphide towards Hydrogen Peroxide. OSCAR HINSBERG (*Ber.*, 1910, 43, 289–290).—When a solution of phenyl sulphide in glacial acetic acid is treated with the equivalent quantity

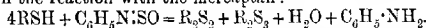
of hydrogen peroxide at the ordinary temperature, phenyl sulphoxide is formed (compare Abstr., 1908, i, 875). If, however, an excess (more than 2 gram-molecules) of hydrogen peroxide is used, and the mixture kept at the room temperature, crystals of phenylsulphone begin to form after a few days. The quantity of sulphone is increased by precipitation with water. Phenylsulphoxide could not be detected in the reaction mixture.

If acetone is used as the solvent (compare Smiles and Gazdar, Trans., 1908, 98, 1833) there is no action between phenyl sulphide and hydrogen peroxide at the ordinary temperature. Reaction only takes place after heating for an hour in a sealed tube at 80–100°, and even in the presence of excess of hydrogen peroxide, only phenyl sulphoxide is formed.

It is assumed that when glacial acetic acid is used as the solvent, it takes part in the reaction, owing to the formation of peracetic acid, $\text{CH}_3\cdot\text{CO}\cdot\text{O}\cdot\text{OH}$. T. S. P.

p-Tolyl Trisulphide. BROR HOLMBERG (*Ber.*, 1910, 43, 226–227).—The author has shown previously (Abstr., 1908, i, 308) that the mercaptans and thionyl chloride interact, with the formation of disulphide, trisulphide, water, and hydrogen chloride. He now finds that thionylaniline also reacts with mercaptans; with ethyl mercaptan, thioglycolic acid, and ethyl thioglycollate, the reaction is so violent that the reagents must be diluted with ether or carbon tetrachloride. It is, however, very difficult to isolate pure products from the reaction mixture.

When *p*-tolyl mercaptan is used, the trisulphide is readily isolated. The mixture of the mercaptan and thionylaniline was heated on the water-bath. After cooling and remaining for a few days, a solid separated, which had m. p. 81–82°, and proved to be *p*-tolyl trisulphide. It forms small plates, thin prisms, or needles, and is pale yellow. The crude solid was contaminated with a yellow oil, which was a mixture of aniline, *p*-tolyl disulphide, and aniline sulphate, the latter compound resulting from the hydrolysis of some of the thionylaniline by water formed in the reaction with the mercaptan:



The following summary shows that the melting points of the thio-diacetic acids and of the *p*-tolyl sulphides show a regularity similar to that observed in many homologous series of carbon compounds. However, the member with an uneven number of sulphur atoms has a higher melting point than the next member with an even number.

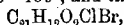
$\text{S}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$..	123°	$p\text{-(C}_6\text{H}_4\text{Me)}_2\text{S}$..	57°
$\text{S}_2(\text{CH}_2\cdot\text{CO}_2\text{H})_2$..	109	$p\text{-(C}_6\text{H}_4\text{Me)}_2\text{S}_2$..	46
$\text{S}_3(\text{CH}_2\cdot\text{CO}_2\text{H})_2$..	124	$p\text{-(C}_6\text{H}_4\text{Me)}_2\text{S}_3$..	82
$\text{S}_4(\text{CH}_2\cdot\text{CO}_2\text{H})_2$..	113	$p\text{-(C}_6\text{H}_4\text{Me)}_2\text{S}_4$..	75

T. S. P.

Phenanthrene Series. XXVI. Conversion of 9-Chloro-10-hydroxyphenanthrene into other Phenanthrene Derivatives. JULIUS SCHMIDT and HERMANN LUMPF (*Ber.*, 1910, 43, 423–438).—9-Chloro-10-hydroxyphenanthrene (Abstr., 1909, i, 35) can be used for VOL. XCVIII. i.

the preparation of 3-nitrophenanthraquinone (*loc. cit.*), of 9:10-chloro-3-bromohydroxyphenanthrene, and other phenanthrene derivatives.

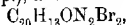
9(10)-Chloro-3-bromo-10(9)-hydroxyphenanthrene, $C_{14}H_9OClBr$, prepared by the action of a carbon disulphide solution of bromine on 9-chloro-10-hydroxyphenanthrene, forms colourless prisms, m. p. 142° , and dissolves in aqueous solutions of alkalis. Its acetyl derivative, $C_{16}H_{10}O_2ClBr$, has m. p. $158-159^\circ$, and the benzoyl derivative,



which crystallises in yellow prisms, m. p. $179-180^\circ$.

When reduced with zinc dust and glacial acetic acid, the bromo-derivative yields 3-bromo-9(10)-hydroxyphenanthrene, $C_{14}H_9OBr$, which could not be crystallised on account of the readiness with which it dissolves in most solvents. Its acetyl derivative, $C_{16}H_{11}O_2Br$, crystallises in pale yellow prisms, m. p. 135° . The position of the bromine atom in the chlorobromohydroxyphenanthrene follows from the readiness with which it can be oxidised by chromic acid to 3-bromophenanthraquinone (Schmidt and Ladner, *Ber.*, 1905, 37, 3571), which appears to exist in yellow and reddish-brown chromo-isomerides.

The dioxime, $C_{14}H_9O_2N_2Br$, prepared by Schmidt and Söll's method (Abstr., 1907, i, 630), forms green, crystalline aggregates, m. p. 212° (decomp.). The monosemicarbazone, $C_{15}H_{10}O_2N_2Br$, forms yellow crystals, m. p. 242° (decomp.), and the monophenylhydrazone,



has m. p. 177° .

The quinone can be reduced to the quinol by means of phenylhydrazine, but it is difficult to isolate the free dihydroxy-compound. Its acetyl derivative, 3-bromo-9:10-diacetoxyphenanthrene, $C_{18}H_{13}O_4Br$, crystallises in colourless needles, m. p. $177-178^\circ$.

3:9(10)-Dihydroxyphenanthrene, $C_{14}H_8(OH)_2$, formed when the 3-bromo-9(10)-hydroxy-compound is fused at 340° with potassium hydroxide, crystallises in colourless prisms, m. p. 175° . The yield is small.

Fuming nitric acid converts the bromophenanthraquinone into a dinitro-derivative, $C_{14}H_6O_6N_2Br_2$, which crystallises in pale yellow, slender needles, m. p. 298° . The monoxime, $C_{16}H_8O_6N_2Br$, forms green prisms, m. p. 196° (decomp.); the semicarbazone, $C_{15}H_8O_6N_3Br$, forms yellowish-brown prisms, m. p. 272° .

The dinitro-quinone condenses with an alcoholic solution of o-phenylenediamine hydrochloride, yielding 3-bromodinitrophenanthraquinazine, $C_{20}H_{10}O_2N_4Br$, as a reddish-white powder, and, when heated on the water-bath with concentrated aqueous ammonia, the quinone yields 3-bromonitroaminophenanthraquinone, $NO_2 \cdot C_{14}H_6BrO_2 \cdot NH_2$, as a dark brown substance, m. p. $280-282^\circ$ (decomp.). The diacetyl derivative, $C_{18}H_{10}O_6N_2Br$, forms an ochre-yellow powder, m. p. 260° (decomp.).

Reduction of the 3-bromodinitrophenanthraquinone with tin and concentrated hydrochloric acid leads to the formation of 3-chlorodiaminophenanthraquinol, which can be readily oxidised by atmospheric oxygen to 3-chlorodiaminophenanthraquinone, $C_{14}H_8ClO_2(NH_2)_2$. The base can be diazotised readily, and the diazo-solution forms azo-dyes with phenols. The dioxime, $C_{14}H_{11}O_2N_2Cl$, forms a deep bluish-black powder, m. p. 264° (decomp.). When the diamino compound is diazo-

tised and the solution boiled, 3-chlorodihydroxyphenanthraquinone, $C_{14}H_8ClO_2(OH)_2$, is obtained as a dark red powder, which is not a substantive dye. The acetyl derivative, $C_{18}H_{11}O_2Cl$, forms brownish-red crystals, m. p. 245°. J. J. S.

Preparation of Carbonatoguaiacol-5-sulphonic Acid and its Salts. F. HOFFMANN, LA ROCHE & Co. (D.R.P. 215050. Compare Abstr., 1909, i, 789).—The preparation of carbonatoguaiacol-5-sulphonic acid and its salts by the action of concentrated sulphuric acid on guaiacol carbonate has been described previously. The free acid forms colourless to dark red, hygroscopic crystals; its cold aqueous solution gives no colour with ferric chloride, but, on heating, carbon dioxide is evolved.

Potassium carbonatoguaiacol-5-sulphonate crystallises in needles, has a neutral reaction, gives no colour with ferric chloride, but by prolonged boiling of its aqueous solution is decomposed into potassium guaiacol-5-sulphonate with evolution of carbon dioxide.

F. M. G. M.

Hydroxyphenylalkylamines and Dihydroxyphenylalkylamines. CARL MANNICH and W. JACOBSON (*Ber.*, 1910, 43, 189–197. Compare Rosentaud, this vol., i, 106; Barger, *Trans.*, 1909, 95, 1123, 2193).—Homologues of *p*-hydroxyphenylamine have been obtained by reducing aldoximes or ketoximes to bases of the type $OMe \cdot C_6H_4 \cdot CH_2 \cdot CHR \cdot NH_2$ or $C_6H_3(OMe)_2 \cdot CH_2 \cdot CHR \cdot NH_2$, and converting these by heating with hydriodic acid into the corresponding phenolic amines. The ketones selected were *p*-methoxybenzyl methyl ketone, 3:4-methylenedioxybenzyl methyl ketone, and 3:4-dimethoxybenzyl methyl ketone; the aldehydes were *p*-methoxyphenylacetaldehyde and 3:4-dimethoxyphenylacetaldehyde.

To obtain *p*-methoxybenzyl methyl ketone, b. p. 136–140°/12 mm., anethole was converted into the dilromide, and this into the bromohydrin, $OMe \cdot C_6H_4 \cdot CH(OH) \cdot CHMeBr$, which on heating with alcoholic potassium hydroxide gave anetholoxide; this, on heating at 220°, undergoes rearrangement to the ketone, $OMe \cdot C_6H_4 \cdot CH_2 \cdot COMe$. The oxime, on reduction with sodium amalgam in acetic acid solution, forms *p*-methoxyphenylisopropylamine, $OMe \cdot C_6H_4 \cdot CH_2 \cdot CHMe \cdot NH_2$, a colourless, strongly alkaline oil, b. p. 158°/25 mm.; the hydrochloride forms large, colourless crystals, m. p. 210°.

p-Hydroxyphenylisopropylamine crystallises in colourless rosettes, m. p. 125–126°; the hydriodide has m. p. 155°.

isoEugenol methyl ether bromohydrin, $C_6H_3(OMe)_2 \cdot CH(OH) \cdot CHMeBr$, has m. p. 78°. It yields the oxide already described by Fourneau and Tiffeneau (*Abstr.*, 1905, i, 591), which readily undergoes rearrangement to 3:4-dimethoxybenzyl methyl ketone, b. p. 198°/20 mm.

3:4-Dimethoxyphenylisopropylamine is an almost colourless oil, b. p. 166–168°/20 mm.; the hydrochloride has m. p. 141°. 3:4-Dihydroxyphenylisopropylamine, $C_6H_3(OH)_2 \cdot CH_2 \cdot CHMe \cdot NH_2$, yields a hydrochloride, m. p. 190–192°.

3:4-Methylenedioxyphenylisopropylamine is a colourless oil, m. p. $157^{\circ}/22$ mm.; the hydrochloride has m. p. $180-181^{\circ}$.

Homovanisaldehyde, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CHO}$, is conveniently prepared by oxidation of *p*-methoxystyrene with mercury oxide and iodine; the oxime forms prisms, m. p. 120° (compare Rosenmund, this vol., i, 106).

The oxime of homoveratraldehyde crystallises in prisms, m. p. $90-91^{\circ}$; the oxime of veratraldehyde has m. p. 82° . On reduction, the oxime yields 3:4-dimethoxyphenylethylamine, a faintly yellow-coloured oil, b. p. $188^{\circ}/15$ mm.; the hydrochloride has m. p. $154-155^{\circ}$.

3:4-Dihydroxyphenylethylamine, $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$, forms a crystalline hydrochloride, decomp. 220° ; it shows a green coloration with ferric chloride.
E. F. A.

Quinocarbonium Perchlorates (II) and the Solvent Action of Chlorinated Ethanes. KARL A. HOFMANN, HEINZ KIRMREUTHER, and A. THAL (*Ber.*, 1910, 43, 183-188. Compare this vol., i, 3).—The triphenylcarbinyl perchlorates crystallise so well that pure preparations are readily obtained from impure carbinols. In accordance with their intense colour, they are easily ionised, so that in solvents such as tetrachloroethane, which is unable to dissociate triphenylmethyl chloride, they still conduct the electric current.

Aurin perchlorate forms doubly refractive, four-sided prisms, which in direct light are orange-red with a light blue reflex. *p*-Trianisylcarbinol perchlorate (compare Gomberg and Cone, this vol., i, 55) crystallises in cinnabar-red, flat needles. It is relatively stable towards water.

Triphenylcarbinyl perchlorate dissolves with a reddish-yellow coloration in tetrachloroethane, and tri-*p*-anisylcarbinol perchlorate with an intense orange coloration. Both solutions conduct electricity, likewise those of the perchlorates in ethylene chloride.

The solubility of the perchlorates in a number of solvents has been compared by the intensity of the colour produced in the saturated solution. The solvents take the following order, the more highly coloured coming first: ethylene chloride, tetrachloroethane, chloroform, dichloroethylene, pentachloroethane, trichloroethylene, perchloroethylene, carbon tetrachloride. The last two or three solvents only become coloured when boiled with the perchlorate. Mercuric chloride dissolves in these solvents in precisely the same order, the solubility being greatest in ethylene chloride and almost nothing in carbon tetrachloride. This confirms the view that the perchlorates are of the nature of metallic salts.

The solvents dissolve sulphur in an altogether different order, ethylene chloride being the least, perchloroethylene the most, effective solvent.
E. F. A.

Action of α -Bromonaphthalene and Magnesium on Certain Carbonyl Compounds. E. SCHURAKOVSKY (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1687-1694).—The interaction of α -bromonaphthalene, magnesium, and acetone yields the compound $\text{MgBr}\cdot\text{O}\cdot\text{CMe}_2\cdot\text{C}_{10}\text{H}_7$.

which is decomposed by water, giving α -naphthylmethylcarbinol (compare Grignard, Abstr., 1901, i, 393). When heated with anhydrous oxalic acid, this alcohol yields β -naphthylpropylene (Grignard, *loc. cit.*), b. p. 251—251.5°/744 mm., D_4^{25} 1.0078, n_D^{25} 1.60684; the molecular refraction, calculated according to the Lorenz and Lorentz formula, is 57.554, which, as is often the case with naphthalene derivatives, differs considerably from the calculated value, 55.387.

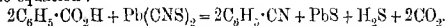
p-Tolyl- α -naphthylmethylcarbinol, $C_6H_4Me \cdot CMe(C_{10}H_7) \cdot OH$, prepared from α -bromonaphthalene, magnesium, and tolyl methyl ketone, was obtained as a dark viscous, impure mass. When heated with anhydrous oxalic acid, this alcohol loses water, giving *alpha*-naphthyl-*p*-tolylethylene, $C_6H_4Me \cdot C(C_{10}H_7) : CH_2$, which is a viscous, faintly yellow liquid, b. p. 224—226°/20 mm., D_4^{25} 1.0693, and combines with 2Br per mol.

Antisl- α -naphthylcarbinol, $OMe \cdot C_6H_4 \cdot CH(C_{10}H_7) \cdot OH$, prepared from α -bromonaphthalene, magnesium, and anisaldehyde, crystallises in small needles or rhombic prisms, m. p. 87°.

α -Naphthylpropenylcarbinol, $CHMe \cdot CH \cdot CH(C_{10}H_7) \cdot OH$, prepared by the interaction of α -bromonaphthalene, magnesium, and crotonaldehyde, is a faintly yellow, viscous liquid, b. p. 204—210°/23 mm.

T. H. P.

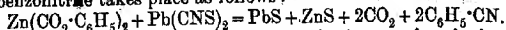
Preparation of Nitriles. E. EMMET REID (*Amer. Chem. J.*, 1910, 43, 162—181).—It was shown by Letts (Abstr., 1872, 1020) that nitriles can be prepared by the action of potassium thiocyanate on organic acids. Krüss (Abstr., 1884, 1314) found in the case of benzonitrile that a better yield could be obtained with lead thiocyanate than with the potassium salt, the reaction being represented by the equation:



In attempting to prepare benzonitrile by Krüss' method, the yield obtained amounted to only 36% of the calculated, and it was observed that only a very small quantity of hydrogen sulphide was evolved. It was therefore considered likely that the hydrogen sulphide might have entered into the reaction and led to the formation of complex products. In order to avoid the formation of hydrogen sulphide, a mixture of lead benzoate and lead thiocyanate was heated, and it was found that, in these circumstances, a much better yield of benzonitrile was obtained. Experiments have been made to ascertain the effect of heating lead, sodium, zinc, and barium benzoates with potassium cyanate, lead cyanate, potassium thiocyanate, lead thiocyanate, barium thiocyanate, lead ferrocyanide, lead cyanide and sulphur, lead ferrocyanide and sulphur, zinc ferrocyanide and sulphur, potassium ferrocyanide and sulphur, and silver cyanide and sulphur. In each case a considerable quantity of benzonitrile was obtained. The results of these experiments are tabulated.

The best method of preparing benzonitrile in the laboratory is to distil a mixture of dry zinc benzoate and dry lead thiocyanate, a yield of 79—91% being thus obtained. A mixture of equivalent quantities of lead ferrocyanide and sulphur may be used instead of the thiocyanate

and, in this case, a yield of about 74% is produced. The formation of the benzonitrile takes place as follows:



On applying this method to other acids, it was found that the nitriles of the three aminobenzoic acids, *p*-nitrobenzoic acid, salicylic acid, and phthalic acid, could not be obtained in this way, but that when lead *m*- or *p*-bromobenzoate was distilled with lead thiocyanate, a satisfactory yield of the bromobenzonitrile was produced in each case.

E. G.

Action of Alcoholic Hydrogen Chloride on *m*-Methylnitrosoaminobenzoic Acid. JOSEF HOUBEN and WALTER BRASSERT (*Ber.*, 1910, 43, 206—212. Compare Abstr., 1909, i, 921).—*m*-Aminobenzoic acid in glacial acetic acid is treated with methyl sulphate. After one hour's heating and keeping for twelve hours, the crystals of *m*-aminobenzoic acid sulphate are removed, and the filtrate is treated with sodium nitrite at 0°, whereby *m*-methylnitrosoaminobenzoic acid, $\text{NO}\cdot\text{NMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, m. p. 179—180° (bath previously at 160°), is obtained, which separates, slightly impure, from water in blood-red leaflets, and is converted after two weeks by alcoholic hydrogen chloride into *ethyl m*-methyaminobenzoate hydrochloride, m. p. 137° (corr.), which is converted into *ethyl m*-methylnitrosoaminobenzoate, m. p. 32°, by nitrous acid at 0°. After twenty-four hours, *m*-methylnitrosoaminobenzoic acid and alcoholic hydrogen chloride yield *m*-methylnitrosoaminobenzoic acid hydrochloride, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NHMe}\cdot\text{HCl}$, m. p. 244°, which is converted by *N*-sodium hydroxide into *m*-methyaminobenzoic acid, m. p. 127° (corr.).

C. S.

New Drugs. V. ALFRED EINHORN (*Annalen*, 1910, 371, 125—131. Compare Abstr., 1900, i, 439, 493; 1903, i, 257; 1908, i, 312).—Mainly a résumé of the work which led to the preparation of novocaine (ω -diethylaminoethyl *p*-aminobenzoate hydrochloride: compare Farbwerke vorm. Meister, Lucius and Brüning, Abstr., 1907, i, 923). As far as can be ascertained, all soluble aromatic esters, with the apparent exception of α -cocaine (compare Willstätter, Abstr., 1896, i, 707), are capable of producing local anaesthesia to a greater or less degree. Generally speaking, the anaesthetic action is destroyed by the introduction of a carboxyl or sulphonyl group into the molecule; other substituents, such as halogen, hydroxyl, alkoxy, nitro, amino, etc., either increase or diminish, but never destroy completely, the activity of an aromatic ester.

W. H. G.

Diethylaminoethyl and Piperidinoethyl *p*-Aminobenzoates. ALFRED EINHORN and EMIL UHLEFELDER (*Annalen*, 1910, 371, 131—142).—An account of the preparation of diethylaminoethyl *p*-aminobenzoate (novocaine), piperidinoethyl *p*-aminobenzoate, and some derivatives of these esters, much of which has appeared already (compare Farbwerke vorm. Meister, Lucius and Brüning, Abstr., 1907, i, 923; 1908, i, 638).

Diethylaminoethyl *p*-aminobenzoate crystallises with $2\text{H}_2\text{O}$ in small needles, m. p. 51°; the anhydrous substance crystallises in plates, m. p. 61°; the following derivatives have been prepared: *mercuri-*

chloride, needles, m. p. 139°; *hydriodide*, small needles, m. p. 121—122°; *mercuri-iodide*, $C_{13}H_{20}O_3N_3, HI, HgI_2$, small, white needles, m. p. 127°; *nitrate*, needles, m. p. 100—101°; *argentonitrate*, needles, m. p. 107°; *sulphate*, prisms, m. p. 170°; *chlorate*,

$C_{13}H_{20}O_3N_3, HClO_3$, needles, m. p. 89°; *borate*, $C_{13}H_{20}O_3N_3, 4B(OH)_3$, small needles, m. p. 159—160°; *trichloroacetate*, prisms, m. p. 89°; *thiocyanate*, prisms, m. p. 83°; *phthalate*, prisms, m. p. 119°; *ethochloride*,

$NH_2 \cdot C_6H_4 \cdot CO_2 \cdot CH_2 \cdot CH_2 \cdot NEt_3Cl, H_2O$, prisms, sinters at 135°, and is completely molten at 180°; the anhydrous ethochloride has m. p. 198° (decomp.); *acetyl* derivative, a viscid oil, the *hydriodide* of which, $C_{15}H_{22}O_3N_3, HI$, crystallises in small rosettes, m. p. 146—147; the *hydrochloride* of the benzoyl derivative,

$C_{20}H_{24}O_3N_3, HCl$, forms small needles, m. p. 189°; the *p*-nitrobenzoyl derivative crystallises in small needles, m. p. 129—130°, and when reduced yields the corresponding *p*-aminobenzoyl derivative, small needles, m. p. 124°, the *hydrochloride* of which, $C_{20}H_{25}O_3N_3, HCl$, crystallises in needles, m. p. 221°.

Piperidinoethyl p-acetylaminobenzoate, $C_{16}H_{22}O_3N_3$, crystallises in needles, m. p. 86—87°; the *hydrochloride* has m. p. 228°; the ester is converted by a hot alcoholic solution of hydrogen chloride into the *dihydrochloride* of piperidinoethyl *p*-aminobenzoate, m. p. 225°.

W. H. G.

Alkylaminoalkyl *p*-Aminobenzoates. ALFRED EINHORN, KARL FIEDLER, CARL LADISCH, and EMIL UHLFELDER (*Annalen*, 1910, 371, 142—161).—The compounds described in this paper were prepared subsequently to novocaine, but not one of them is more suitable than this substance for the purpose of producing local anaesthesia. They are all obtained by the reduction of the corresponding *p*-nitrobenzoates, which are prepared by the action of *p*-nitrobenzoyl chloride on the requisite alkamine.

Dimethylaminoethyl p-nitrobenzoate,

$NO_2 \cdot C_6H_4 \cdot CO_2 \cdot CH_2 \cdot CH_2 \cdot NMe_2$, prepared by heating dimethylaminoethyl alcohol with *p*-nitrobenzoyl chloride at 130°, crystallises in slender, matted needles, m. p. 58—59°; when reduced with tin and hydrochloric acid, it yields the corresponding amino-compound, $C_{11}H_{16}O_3N_3$, crystallising in large prisms, m. p. 121°, the *hydrochloride* of which, $C_{11}H_{17}O_3N_3, HCl$, forms small, slender needles, m. p. 185—186°.

Diisopropylaminoethyl p-nitrobenzoate is an oil; the *hydrochloride*, $C_{15}H_{22}O_4N_3, HCl$, crystallises in small needles, m. p. 136·5°; the corresponding amino-compound, $C_{15}H_{24}O_3N_3$, crystallises in slender needles, m. p. 48°, and forms a *hydrochloride*, crystallising in prisms, m. p. 195°.

Diisobutylaminoethyl p-nitrobenzoate is an oil; the *hydrochloride*, $C_{17}H_{26}O_4N_3, HCl$, forms slender, felted needles, m. p. 160—161°; the amino-compound, $C_{17}H_{28}O_3N_3$, small, slender needles, m. p. 84—85°, forms a *hydrochloride*, which crystallises in prisms, m. p. 195—196°.

Diisoamylaminoethyl p-nitrobenzoate is an oil; the *hydrochloride*,

$C_{19}H_{20}O_4N_2 \cdot HCl$, crystallises in small needles, m. p. 123—124°; the amino-compound, $C_{15}H_{22}O_2N_2$, leaflets, m. p. 44—45°, forms a *hydrochloride*, crystallising in needles, m. p. 154°.

Diethylaminomethylmethylethylcarbinol, $NEt_2 \cdot CH_2 \cdot CMeEt \cdot OH$, prepared by the action of diethylamine on the corresponding chloro-compound, is an oil, b. p. 71—73°/15.5 mm.; the *p-nitrobenzoate* is an oil, the *hydriodide* of which, $C_{16}H_{24}O_4N_2 \cdot HI$, forms pale yellow crystals, m. p. 167°; the *p-aminobenzoate* is a pale yellow oil, the *picrate* of which, $C_{22}H_{26}O_8N_4$, is a pale yellow, crystalline powder, m. p. 121°.

Piperidinomethylmethylethylcarbinol, $NC_5H_{10} \cdot CH_2 \cdot CMeEt \cdot OH$, is a colourless oil, b. p. 101—104°/18 mm.; the *p-nitrobenzoate* is a viscid, yellowish-brown oil, the *hydriodide* of which, $C_{17}H_{24}O_4N_2 \cdot HI$, crystallises in yellow leaflets, m. p. 190°; the *p-aminobenzoate* is an oil, crystalline salts of which could not be obtained.

Diethylaminomethylethylcarbinol has b. p. 197—200° (compare Paal and Weidenkaff, Abstr., 1906, i, 236); the *p-nitrobenzoate* is an oil, the *hydriodide* of which, $C_{17}H_{26}O_4N_2 \cdot HI$, crystallises in yellow prisms, m. p. 154°; the *hydrochloride* of the oily *p-aminobenzoate*, $C_{17}H_{28}O_2N_2 \cdot HCl$, forms rhomboidal crystals, m. p. 166—167°.

Tetraethyldiaminoisopropyl p-nitrobenzoate,
 $NO_2 \cdot C_6H_4 \cdot CO_2 \cdot CH(CH_3 \cdot NEt_2)_2$,
 forms yellow crystals, m. p. 41°; the *dihydrochloride* crystallises in slender, felted needles, m. p. 198°; the *p-aminobenzoate*, $C_{18}H_{31}O_2N_3$, crystallises in colourless leaflets, m. p. 50°; the *dihydrochloride* forms faintly yellow, slender needles, m. p. 222°.

Dipiperidinoisopropyl p-nitrobenzoate,
 $NO_2 \cdot C_6H_4 \cdot CO_2 \cdot CH(CH_2 \cdot NC_5H_{10})_2$,
 is an oil; the *dihydriodide* crystallises in lemon-yellow, slender needles, m. p. 232°; the corresponding amino-compound, $C_{20}H_{31}O_2N_3$, forms colourless prisms, m. p. 137.5°, the *dihydrochloride* of which crystallises in slender needles, m. p. 261°.

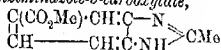
The *p-nitrobenzoate* of α -diethylaminopropane- $\beta\gamma$ -diol,
 $NEt_2 \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot CO_2 \cdot C_6H_4 \cdot NO_2$ or
 $NEt_2 \cdot CH_2 \cdot CH(CO_2 \cdot C_6H_4 \cdot NO_2) \cdot CH_2 \cdot OH$,
 is an oil; the *hydrochloride* is a microscopic, crystalline powder, m. p. 152°; the corresponding amino-ester is an oil; the *di-p-nitrobenzoate*, $C_{21}H_{28}O_8N_4$, forms small, yellow needles, m. p. 90—92°; the *di-p-aminobenzoate* has m. p. 132°; the *hydrochloride*, $C_{21}H_{27}O_4N_3 \cdot HCl$, is a crystalline powder, m. p. 185°. The *p-nitrobenzoate* of the corresponding piperidino-compound, $C_{16}H_{20}O_4N_2$, forms leaflets, m. p. 60—63°; the *hydrochloride* crystallises in white needles, m. p. 212°; the *p-aminobenzoate*, $C_{15}H_{22}O_3N_2$, crystallises in prisms, m. p. 91°; the *hydrochloride* forms white needles, m. p. 206°; the *di-p-nitrobenzoate*, $C_6NH_{10} \cdot CH_2 \cdot CH(CO_2 \cdot C_6H_4 \cdot NO_2) \cdot CH_2 \cdot CO_2 \cdot C_6H_4 \cdot NO_2$, crystallises in pale, yellow prisms, m. p. 108°; the *di-p-aminobenzoate* crystallises in prisms, m. p. 127°; the *hydrochloride*, $C_{22}H_{27}O_4N_3 \cdot HCl$, forms small needles, m. p. 210.5°.

W. H. G.

Esters and Alkylamino-esters of 3:4-Diaminobenzoic Acid. ALFRED EINHORN and EMIL UHLFELDER (*Annalen*, 1910, 371, 162—179. Compare Einhorn, Abstr., 1908, i, 639).—The compounds

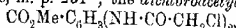
described in this paper were prepared with the object of obtaining derivatives of alkyl 3:4-diaminobenzoates yielding salts with a neutral reaction, which could consequently be employed as anæsthetics. The esters of 3:4-diaminobenzoic acid when boiled with organic acids yield esters of 2-alkylbenzimidazole-5-carboxylic acid, and when treated with acetyl chloride yield the corresponding dichloroacetyl derivatives; the latter substances interact with secondary bases, for example, piperidine, yielding the dipiperidinoacetyl compounds.

Methyl 2-methylbenzimidazole-5-carboxylate,

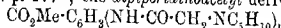


crystallises in needles, m. p. 172°; the *hydrochloride* forms small needles, m. p. 257°; the *ethyl* ester crystallises in needles, m. p. 180°.

Methyl 2-ethylbenzimidazole-5-carboxylate, $\text{C}_{11}\text{H}_{12}\text{O}_2\text{N}_2$, crystallises in needles, m. p. 141°; the *hydrochloride* has m. p. 252°. The *dibenzoyl* derivative of methyl 3:4-diaminobenzoate, $\text{C}_{22}\text{H}_{18}\text{O}_2\text{N}_2$, crystallises in small, white needles, m. p. 231°; the *dichloroacetyl* derivative,

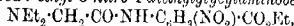


forms needles, m. p. 177°; the *dipiperidinoacetyl* derivative,



has m. p. 108°.

Ethyl 3-nitro-4-chloroacetylaminobenzoate, $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_2\text{Cl}$, crystallises in small, yellow needles, m. p. 102°. *Ethyl 3-nitro-4-piperidinoacetylaminobenzoate* crystallises in yellow needles, m. p. 70–71°, and when reduced with tin and hydrochloric acid below 35° yields the corresponding amino-compound, $\text{C}_{12}\text{H}_{23}\text{O}_2\text{N}_3$, small needles, m. p. 103°, the *hydrochloride* of which crystallises in leaflets, m. p. 204°, whilst at a higher temperature it is converted into *ethyl 2-piperidinomethylbenzimidazole-5-carboxylate*, $\text{C}_{16}\text{H}_{21}\text{O}_2\text{N}_3$, an oil, the *dihydrochloride* of which crystallises in needles, m. p. 227°. The following compounds are similarly prepared: *ethyl 3-nitro-4-diethylglycylaminobenzoate*,



yellow needles, m. p. 71°; *ethyl 3-amino-4-diethylglycylaminobenzoate*, small needles, m. p. 64°; *hydrochloride*, needles, m. p. 194°; *ethyl 2-diethylaminomethylbenzimidazole-5-carboxylate*, $\text{C}_{15}\text{H}_{21}\text{O}_2\text{N}_3$, pointed needles, m. p. 67°; *hydrochloride*, small needles, m. p. 173°; *dihydrochloride*, m. p. 199°.

Chloroethyl 3:4-diaminobenzoate, $\text{C}_6\text{H}_3(\text{NH}_2)_2\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$, is obtained by acting on a mixture of 3:4-diaminobenzoic acid and ethylene chlorohydrin with hydrogen chloride in the presence of a small quantity of concentrated sulphuric acid; it crystallises in needles, m. p. 80°, and, when heated with diethylamine under pressure at 100–120°, yields the corresponding *diethylaminoethyl* ester, an oil, the *hydrochloride* of which, $\text{C}_{15}\text{H}_{21}\text{O}_2\text{N}_3\cdot\text{HCl}$, forms needles, m. p. 163°; the *picrate* crystallises in yellow needles, m. p. 189–190°. The *diethylaminoethyl* ester undergoes the following changes: (1) with glyoxal, it yields *diethylaminoethyl quinoxaline-6-carboxylate*, an oil, the *hydrochloride* of which, $\text{C}_{15}\text{H}_{21}\text{O}_2\text{N}_3\cdot\text{HCl}$, crystallises in needles, m. p. 187°; (2) when treated with sodium nitrite and hydrochloric acid, it yields *diethylaminoethyl 3:4-aziminobenzoate hydrochloride*, $\text{C}_{13}\text{H}_{19}\text{O}_2\text{N}_3\cdot\text{HCl}$, small needles, m. p. 150–151°; (3) it condenses

with *p*-dimethylaminobenzaldehyde, yielding a *substance*, which crystallises in yellow needles, m. p. 161°, and with benzaldehyde, yielding an oily *substance*, the *hydrochloride* of which crystallises in prisms, m. p. 190°.

Piperidinoethyl 3:4-diaminobenzoate crystallises in needles, m. p. 103°, when heated with glacial acetic acid, it yields *piperidinoethyl 2-methylbenzimidazole-5-carboxylate*, $C_{16}H_{21}O_2N_3$, needles, m. p. 159–160°, the *hydrochloride* and *dihydrochloride* of which crystallise in needles, m. p. 162–163° and 262° respectively.

Diethylaminoethyl 3-nitro-4-dimethylaminobenzoate, prepared from 3-nitro-4-dimethylaminobenzoic acid and diethylaminoethanol, is an oil; the corresponding *amino-compound*, also an oil, forms a *hydrochloride*, $C_{15}H_{25}O_2N_3 \cdot HCl$, which crystallises in needles, m. p. 164°.

Methyl 3:4-tetramethyldiaminobenzoate dihydriodide, prepared by heating methyl 3-amino-4-dimethylaminobenzoate with methyl iodide and methyl alcohol under pressure at 100°, crystallises in needles, m. p. 109–110°; the *dihydrobromide*, $C_{12}H_{18}O_2N_2 \cdot 2HBr$, crystallises in needles, m. p. 205°; the corresponding *diethylaminoethyl ester* is an oil; the *hydrochloride*, $C_{17}H_{29}O_2N_3$, crystallises in small, white needles, m. p. 140–141°.

W. H. G.

Isomerism of Anils (Schiff's Bases). OTTO ANSELMINO (*Ber.*, 1910, 43, 462–463. Compare Manchot and Furlong, *Abstr.*, 1900, i, 805; this vol., i, 33; Anselmino, *Abstr.*, 1906, i, 13; 1907, i, 913; Knoevenagel and Schrötter, *Abstr.*, 1905, i, 64).—Polemical.

J. J. S.

Differences between Cinnamic Acid from Storax and Synthetical Cinnamic Acid. C. N. RIIBER and V. MORITZ GOLDSCHMIDT (*Ber.*, 1910, 43, 453–462. Compare E. Erlenmeyer, *jun.*, *Abstr.*, 1907, i, 318; 1909, i, 156, 647, 648).—Although cinnamic acid from storax differs so materially in habit from the synthetical acid, it is shown that the characteristic crystallographic constants are the same for the two acids. The chief differences are (a) the extremely thin plates in which the synthetical acid crystallises; (b) the absence of definite faces in the crystals of the synthetical acid; the plates as a rule have a crinkled edge.

As the synthetical acid when repeatedly crystallised approaches the habit of the storax acid, the conclusion is drawn that the former acid is identical with the storax acid, but contains a small amount of an impurity which is gradually removed by repeated crystallisation. The presence of this impurity retards to an enormous extent the development of the crystals in the direction normal to the face $b\{010\}$.

By careful fractionation of the ethyl ester of the synthetical acid, it has been found possible to isolate a fraction b. p. about 120°/0.2 mm., which when hydrolysed gives an acid containing about 9% Cl. This acid is probably an impure chlorocinnamic acid, and it is shown that when this impure acid or when small amounts of either *o*- or *p*-chlorocinnamic acids are added to the acid from storax, they alter its crystalline habit and transform it into the characteristic crystals of the synthetical acid. The synthetical acid is thus the same

acid as that from storax, but contains a small amount of a chloro-acid which completely alters its crystalline appearance.

Erlenmeyer's hetero-acid contains a larger proportion of the chloro-acid than does the synthetical acid.

Erlenmeyer states that specimens of benzaldehyde which are free from chlorine yield the synthetical acid. It is shown that small amounts (0.3%) of *o*-nitrocinnamic acid have the same effect on the crystalline habit of the storax acid as larger amounts of the chloro-acids.

Erlenmeyer's α - and β -cinnamic acids are regarded as dimorphous forms (compare Lehmann, *Zeitsch. Kryst. Min.*, 1885, 10, 329).

J. J. S.

Transformations of *allo*-Cinnamic and *iso*Cinnamic Acids. CARL LIEBERMANN and H. TRUCKSÄSS (*Ber.*, 1910, 43, 411—414. Compare this vol., i, 36).—It is shown that when *allocinnamic* or *isocinnamic* acid of m. p. 58° is crystallised from carefully rectified light petroleum (b. p. 30—40°), crystals of the *iso*-acid, m. p. 42°, can usually be obtained if proper precautions are taken. The method consists in introducing a comparatively dilute solution of the acid into a glass tube by means of a suitable funnel, and then boiling the solution for some little time, so that the walls of the tube are thoroughly purified, and also that the solution may be concentrated. The tube is then sealed, and when placed in ice-cold water or in a freezing mixture, crystals of the acid m. p. 42° separate. These occasionally become transformed into the less fusible acids during transference from the tube.

J. J. S.

Mechanism of the Transformation of α -Hydroxy- β -unsaturated Acids into the Isomeric γ -Keto-acids. EMIL ERLERMAYER (*Festschrift Otto Wallach*, 1909, 404—413).—A discussion on the course of the intramolecular rearrangement of α -hydroxy- β -unsaturated acids into γ -ketones (compare Fittig, *Abstr.*, 1897, i, 14; 1898, i, 196), based on the author's investigations (compare *Abstr.*, 1898, i, 668; 1903, i, 32, 414; 1904, i, 500, 892, 1025). W. H. G.

[Preparation of Triphenylmethane Colouring Matters from Diortho-substituted Benzaldehydes.] ANILINFARBEN- & EXTRAKT-FABRIKEN VORM. J. R. GEIGY (D.R.-P. 213502. Compare *Abstr.*, 1908, i, 986).—It has been shown previously that the diortho-substituted benzaldehydes when employed in the production of triphenylmethane dyes yield colours of remarkable depth and fastness; it is now found that these properties are enhanced when the two ortho-substituents consist of different halogen atoms. The following new aldehydes are described:

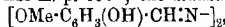
2-Chloro-6-bromobenzaldehyde, prepared from 2-chloro-6-bromotoluene, forms colourless, spear-shaped crystals, m. p. 68°.

2-Chloro-4:6-dibromo-5-aminobenzaldehyde, m. p. 124°, a colourless, crystalline powder, is obtained by the bromination in aqueous suspension of 2-chloro-5-aminobenzaldehyde. *2:4:6-Tribromo-5-aminobenzaldehyde*, m. p. 136—137°. *2-Chloro-4:6-dibromo-5-hydroxybenzaldehyde* crystallises in dark yellow needles, and has m. p. 116°.

F. M. G. M.

p-Methoxysalicylaldehyde. PAUL FRIEDLÄNDER (*Monatsh.*, 1909, 30, 879—881).—Since *p*-methoxysalicylaldehyde (*o*-hydroxyanisaldehyde), prepared by the action of sodium hydroxide on 4-methoxy-2-keto-1-indoxylbenzene (compare Friedländer and Schuloff, *Abstr.*, 1908, i, 674), did not have the properties of the *o*-hydroxyanisaldehyde described by Tiemann and Parrisius (compare *Abstr.*, 1881, 270), the compound has been prepared by the method employed by these investigators, also by the action of methyl sulphate on 2:4-dihydroxybenzaldehyde, and found to be identical with that derived from 4-methoxy-2-keto-1-indoxylbenzene. It is shown, further, that the substance obtained by Goulding and Pelly from *Chlorocodon Whitei* (*Proc.*, 1908, 24, 62) is *o*-hydroxyanisaldehyde.

o-Hydroxyanisaldehyde has m. p. 41°; the oxime has m. p. 138°; the phenylhydrazone has m. p. 138°; the *aldazine*,



forms small, greenish-yellow crystals, m. p. 220°.

W. H. G.

Orthovanillin [2-Hydroxy-3-methoxybenzaldehyde] and its Derivatives. FRANCIS A. M. NOELTING (*Bull. Soc. Ind. Mulhouse*, 1909, 79, 401—430).—The compound described by Tiemann and Koppe as *β*-*m*-methoxysalicylaldehyde (compare *Abstr.*, 1882, 54) is definitely shown to be 2-hydroxy-3-methoxybenzaldehyde, for, when treated with acetic anhydride, it yields 8-methoxycoumarin.

A large number of hydroxy- and methoxy-derivatives of benzaldazine and benzylideneaniline have been prepared with the object of ascertaining the effect of these groups on the colour of the substance. It is found that the para-derivatives of benzaldazine are the most highly-coloured, whilst the ortho-substitution products of benzylideneaniline are more intensely coloured than the corresponding para-isomerides; for example, vanillaldazine is golden-yellow, whilst 2-hydroxy-3-methoxybenzylaldazine is lemon-yellow; 2-hydroxy-3-methoxybenzylideneaniline is orange, whilst the 4-hydroxy-isomeride is pale yellow. The ortho-, meta-, and para-hydroxy-derivatives of benzylideneaniline are lemon-yellow, white, and pale yellow respectively; the methyl ethers are all colourless, although the hydrochlorides are lemon-yellow; the methoxy-derivatives of the methyl ethers are not coloured, although the introduction of a methoxy-group into the hydroxy-derivatives increases the colour. Derivatives of benzylideneaniline containing a hydroxy- or methoxy-group are rendered more intensely coloured by the introduction of a hydroxy-group.

2-Hydroxy-3-methoxybenzaldehyde crystallises in pale yellow needles, m. p. 45·5°, b. p. 265—266°; it dyes wool an intense yellow, and silk a pale yellow; the m. p.'s of various mixtures of this compound with vanillin are recorded; the sodium salt, $\text{C}_8\text{H}_7\text{O}_3\text{Na}\cdot\text{H}_2\text{O}$, crystallises in lemon-yellow plates; the benzoate crystallises in small, white needles, m. p. 74—75°; the oxime crystallises in white needles; the phenylhydrazone, $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}\cdot\text{N}\cdot\text{NHPh}$, forms colourless needles, m. p. 130—131°; the phenylmethylhydrazone forms colourless crystals, m. p. 62°. The methyl ether, $\text{C}_8\text{H}_7(\text{OMe})_2\cdot\text{CHO}$, crystallises in white needles, m. p. 52—53°, and dissolves in concentrated sulphuric acid to a blood-red solution; the finely-divided substance produces

violent sneezing; the *oxime* has m. p. 98–99°; the *phenylhydrazone*, m. p. 138°, is white. The parent substance couples with diazo compounds, forming compounds of the type

$$\begin{array}{c} \text{C}(\text{CHO})\text{:CH}-\text{C}\cdot\text{N}_2\text{R} \\ | \\ \text{C}(\text{OH})\text{:C}(\text{OMe})\text{CH} \end{array}$$

and forms *condensation products* with the following bases, the colours of which only are given: α -naphthylamine, scarlet; β -naphthylamine, crimson; *p*-toluidine, orange; *p*-anisidine, yellowish-orange; *p*-phenetidine, yellowish-orange; *o*-chloroaniline, bright red; dichloroaniline, bright red; *p*-nitroaniline, orange-red; *m*-nitrotoluidine, orange-yellow; *p*-phenylenediamine, scarlet; benzidine, brick-red.

o-Methoxybenzylideneaniline, m. p. 44°, is white; the *meta*-isomeride is also white; 3:4-dihydroxybenzylideneaniline, m. p. 172°, is bright yellow, whilst the *dimethyl ether*, m. p. 81°, is white; 2-hydroxy-3-methoxybenzylideneaniline, m. p. 84–85°, is orange, whilst the *methyl ether*, m. p. 82.5°, is white; 4-hydroxy-3-methoxybenzylideneaniline, m. p. 152–153°, is pale yellow.

m-Hydroxybenzaldazine, m. p. 204–205°, is pale yellow; 2-hydroxy-3-methoxybenzaldazine, m. p. 198–199°, is lemon-yellow, whilst the *methyl ether*, m. p. 151°, is pale yellow.

Dimethylaniline condenses with 2-hydroxy-3-methoxybenzaldehyde and 2:3-dimethoxybenzaldehyde, yielding 4':4'-tetramethyldiamino-2''-hydroxy-3''-methoxytriphenylmethane, m. p. 144°, and 4':4'-tetramethyldiamino-2'' : 3''-dimethoxytriphenylmethane, m. p. 130–131°, respectively; the *hydrochlorides* are green and bluish-green respectively.

8-Methoxycoumarin forms inodorous, white crystals, m. p. 89°.

W. H. G.

Carbonyl Group in the Nascent State. PAVEL IW. PETRENKO-KRITSCHENKO (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1698–1703).—A reply to Stewart and Baly (compare Abstr., 1907, i, 220).

T. H. P.

Tetrabromocyclopentenenedione. C. LORING JACKSON and H. A. FLINT (*Amer. Chem. J.*, 1910, 43, 135).—Jackson and Russe (Abstr., 1906, i, 290) found that by the action of fuming nitric acid and bromine on tetrabromo-*o*-benzoquinone, two substances were produced, one, yellow, m. p. 142°, and the other, white, m. p. 144–146°. The present investigation was undertaken with a view to the further study of these compounds.

The white substance could not again be obtained, but oxalic acid was invariably produced.

The yellow compound has been found to be identical with Henle's tetrabromocyclopentene-1:3-dione (Abstr., 1907, i, 223), and is shown to have the constitution

$$\text{CO} \begin{array}{c} \text{CBr}_2 \cdot \text{CO} \\ \diagdown \quad \diagup \\ \text{CBr} = \text{CBr} \end{array}$$

It is readily decom-

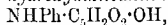
posed by boiling water or alcohol, but is remarkably stable towards acids or oxidising agents, and can be boiled for several hours with fuming nitric acid without undergoing visible change. When the compound is treated with solution of sodium carbonate for several days at the ordinary temperature, it is converted into dibromomaleic

acid and methylene dibromide. The action of sodium methoxide on the compound also results in the formation of dibromomaleic acid.

By the action of aniline on tetrabromocyclopentene-1:3-dione, there are produced *tribromoanilinocyclopentenedione*, $\text{NHPh}\cdot\text{C}_5\text{O}_2\text{Br}_3$, m. p. 178° , which crystallises in yellow needles, and *hydroxyanilinocyclopentenedione*, $\text{NHPh}\cdot\text{C}_5\text{O}_2(\text{OH})\cdot\text{NHPh}$, which forms a dark red, amorphous powder, and does not melt below 300° .

When tetrabromocyclopentenedione is reduced with sulphurous acid, *dibromodiketocyclopentene*, $\text{C}_5\text{H}_2\text{O}_4\text{Br}_2$, m. p. 151° , is obtained, which crystallises in pale yellow plates, and, on treatment with bromine, is reconverted into tetrabromocyclopentenedione. Phenylhydrazine reacts with dibromocyclopentenedione with formation of a brown, amorphous substance, which does not melt below 300° . When dibromocyclopentenedione is treated with aniline, *bromoanilinocyclopentenedione*, $\text{NHPh}\cdot\text{C}_5\text{H}_2\text{O}_4\text{Br}$, m. p. 121° (decomp.), is produced, which forms slender, yellow needles, and is converted by sodium carbonate solution into 1-anilino- Δ^1 -cyclopropen-3-one, $\text{NHPh}\cdot\text{C}\begin{smallmatrix} \text{CO} \\ \diagup \\ \text{CH} \end{smallmatrix}$, m. p. 221° (decomp.), which crystallises in yellow needles.

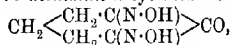
By the action of methyl alcohol on tetrabromodiketocyclopentene, *tribromodiketomethoxycyclopentene*, $\text{OMe}\cdot\text{C}_5\text{O}_2\text{Br}_3$, m. p. 67° , is obtained, which forms white, slender needles. The corresponding ethoxy compound, m. p. 110° , crystallises in small, white needles, and is converted by aniline into *hydroxydiketoanilinocyclopentene*,



m. p. 140° (decomp.), a red, amorphous substance, which yields an acetyl derivative, m. p. 150° (decomp.), as a pale brown, amorphous powder.

E. G.

Nitrosation of the Simplest Cyclic Ketones. WALTHER BORSCHKE (*Festschrift Otto Wallach*, 1909, 301—312).—*cycloHexanone* is converted by amyl nitrite in the presence of a small quantity of acetyl chloride into 1:3-dioximino-2-cyclohexanone,



which crystallises in glistening, yellow needles, m. p. above 200° (decomp.), and is decomposed by water, alcohol, and dilute acids; the corresponding triketone could not be isolated. The dioxime when treated with an alcoholic solution of sodium ethoxide and benzoyl chloride yields a substance, $\text{C}_{20}\text{H}_{22}\text{O}_5\text{N}_3$ (I), crystallising in colourless needles, m. p. $92-93^\circ$; benzoylation in the presence of pyridine leads to the formation of a *dibenzoate*, $\text{CH}_2\begin{smallmatrix} \text{CH}_2\cdot\text{C}(\text{OBz})\cdot\text{N} \\ \diagup \\ \text{CH}_2\cdot\text{C}(\text{OBz})\cdot\text{N} \end{smallmatrix}\text{CO}$ (II), which crystallises in slender, yellow needles, m. p. $170-172^\circ$ (decomp.), and when boiled with an aqueous solution of sodium hydroxide is probably decomposed, thus: $\text{C}_{20}\text{H}_{16}\text{O}_5\text{N}_2 + 4\text{NaOH} = \text{CN}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CN} + \text{Na}_2\text{CO}_3 + 2\text{Ph}\cdot\text{CO}_2\text{Na} + 2\text{H}_2\text{O}$. An alcoholic solution of phenylhydrazine converts the dioxime into 1:2:3-triketocyclohexanetriphenylhydrazone, $\text{C}_{24}\text{H}_{24}\text{N}_6$, which crystallises in slender needles, m. p. $182-183^\circ$. The dioxime interacts with *o*-phenylenediamine, yielding

1-oximino-1:2:3:4-tetrahydrophenazine, $C_6H_4 \begin{smallmatrix} N:C \cdot C(N \cdot OH) \cdot CH_2 \\ N:C \cdot CH_2 \cdot CH_2 \end{smallmatrix}$, small, glistening, brown crystals, m. p. 216—218°.

3:5-Dioximino-1-methyl-4-cyclohexanone, $C_7H_{10}O_3N_2$, prepared from 4-methylcyclohexanone, crystallises in pale yellow leaflets, turns brown at 180°, and decomposes suddenly at 208°. The following derivatives are prepared by the methods just described: *dibenzoate*, small, pale yellow needles, decomposing at 172°; 3:4:5-triketo-1-methylcyclohexanetriphenylhydrazine, $C_{25}H_{22}N_6$, small, slender, yellow needles, m. p. 184°; 1-oximino-3-methyl-1:2:3:4-tetrahydrophenazine, $C_{13}H_{13}ON$,

small, glistening, yellow needles, m. p. 210—211°. The parent substance is converted (1) by a cold solution of phenylhydrazine in glacial acetic acid into 3:5-dioximino-1-methylcyclohexan-4-onephenylhydrazine, $C_{13}H_{10}O_2N_4$, a crystalline, orange powder, m. p. 220° (decomp.); (2) an alcoholic solution of semicarbazide hydrochloride and sodium acetate into the *semicarbazone*, $C_8H_{12}O_2N_2$, which crystallises in spherical aggregates of small, colourless needles and decomposes at 200°; (3) by an alcoholic solution of hydroxylamine hydrochloride and sodium acetate into the corresponding *trioxime*, a colourless syrup, the *dibenzoate* (?) of which, $C_{21}H_{14}O_6N_3$, crystallises in small, colourless needles, m. p. 175°.

1:3-Dioximino-2-cyclopentanone, $C_6H_8O_3N_2$, prepared from cyclopentanone, crystallises in flat, yellow needles, and decomposes suddenly at 215°.

W. H. G.

Catalytic Preparation of Aromatic Ketones. JEAN B. SENDERENS (*Compt. rend.*, 1910, 150, 111—112. Compare Abstr., 1909, i, 286, 627; this vol., i, 11).—The following aromatic ketones are readily obtained by the method already described, namely: acetophenone, propiophenone, phenyl propyl ketone, phenyl isopropyl ketone, phenyl isobutyl ketone. To obtain a good yield, it is necessary to employ 3 mols. of the fatty acid to 1 mol. of benzoic acid, and to maintain the temperature of the catalyst at 380—460°. The product is always accompanied by smaller quantities of the symmetrical aliphatic ketone. Benzoic acid may be replaced by its anhydride. Benzophenone could not be obtained by this method. W. O. W.

Additive Compounds of Ketones and Quinones with Acids and Phenols. KURT H. MEYER (*Ber.*, 1910, 43, 157—164. Compare Abstr., 1908, i, 731; 1909, i, 395).—Whereas acetophenone only forms colourless double salts with metallic chlorides, benzophenone in many cases yields light yellow compounds. A yellow *nitrate*, $C_{15}H_{10}O \cdot HNO_3$, has been isolated, whilst the faintly yellow-coloured solution of benzophenone in sulphuric acid undoubtedly contains a coloured sulphate. Benzophenone has, although to a much less extent, the same properties of halochromism as distyryl ketone. The coloured compounds of benzophenone could not be isolated, but those of fluorenone are more characteristic. Two series of double salts are formed, the one a deep violet, represented by the compound with aluminium bromide, and the other, orange in colour. The solution in

sulphuric acid apparently contains both forms, as the deep violet solution becomes orange-red on the gradual addition of water, and finally colourless when the fluorenone separates.

Fluorenone also combines with phenols, forming deeply-coloured products. With α -naphthol, two compounds are formed: an orange-yellow derivative from two molecules of fluorenone and one molecule of α -naphthol, and a red substance from one molecule of each component.

Similar compounds could not be obtained from distyryl ketone. Dianisylidenacetone, however, dissolves in phenol with an intense yellow coloration, and forms with α -naphthol a crystalline, orange-yellow compound, containing three molecules of α -naphthol to two molecules of the ketone.

These compounds of ketones and quinones with phenols are regarded as belonging to the same class of additive compounds as those with acids, metallic chlorides, and sulphur dioxide. Both classes possess a deep colour, pronounced crystallising power, and are easily resolved into their components by water, or when heated in solvents; their formation is exothermic. They are regarded as loose additive products to the quinonoid or ketone oxygen atom. *Fluorenone nitrate* forms orange-red needles; the *trichloroacetate* gives orange needles, m. p. 58° ; the *mercurichloride*, $C_{13}H_8O \cdot (HgCl_2)_2$, separates in lustrous, orange needles. The *stannichloride*, $(C_{13}H_8O)_3 \cdot SnCl_4$, forms brownish-yellow crystals. With sulphur dioxide a substance crystallising in orange needles is obtained, containing between 1 and $1\frac{1}{2}$ mols. of sulphur dioxide. *Fluorenone aluminium bromide* separates in dark red, almost black crystals. The compound, $2C_{13}H_8O \cdot C_{10}H_8O$, produced on heating with α -naphthol, crystallises in long, orange needles, m. p. $66-67^\circ$. In presence of an excess of α -naphthol this is converted into $C_{13}H_8O \cdot C_{10}H_8O$, separating in stout, red crystals, m. p. 89° .

The compound of 2 mols. of dianisylidenacetone and 3 mols. of α -naphthol separates in long, orange needles, m. p. 69° . Dianisylidenacetone and sulphur dioxide form an orange-yellow solution, giving rise to orange-yellow needles when concentrated.

Phenanthraquinone trichloroacetate, $C_{14}H_8O_2 \cdot C_2HCl_3$, crystallises in sealing-wax red needles, m. p. 138° . E. F. A.

Occurrence of β -Pinene and *l*-Pinocamphone in Hyssop Oil, and Some Observations on Isomerides in the Pinene Series. EDUARD GILDENEISTER and HUGO KÖHLER (*Festschrift Otto Wallach*, 1909, 414-438).—An account of part of this investigation has appeared previously (compare Schimmel & Co., Abstr., 1908, i, 666). *l*-Pinocamphone, obtained directly from hyssop oil, has b. p. $212-213^\circ/752$ mm., D_{25}^{25} 0.9662, n_D^{25} 1.47421, α_D^{25} -13.7° , whilst a sample prepared by reducing the dibromide had b. p. $212.5-213.5^\circ/749$ mm., D_{25}^{25} 0.9679, n_D^{25} 1.47509, n_D^{20} 1.47343, α_D^{20} -19.33° ; the dibromide has $[\alpha]_D^{25}$ -49.24° in ether; the *semicarbazone* has m. p. $228-229^\circ$; a small quantity of a second *semicarbazone*, m. p. about $182-183^\circ$, was also obtained; the *oxime* is a colourless oil, b. p. $105-110^\circ/4$ mm., which deposits well-defined crystals, m. p. about

37–38°, when kept for some time. The ketone is reduced by alcohol and sodium, yielding *l-pinocampheol*, long, matted needles, m. p. 67–68°, b. p. 217–218°, n_D^{20} 1.48335, n_D^{25} 1.48420, n_D^{30} 1.48335; the corresponding *phenylurethane* crystallises in silky needles, m. p. 76–77°. *l-Pinonic acid*, obtained by the oxidation of the ketone, is identical with that described by Barbier and Grignard (compare Abstr., 1908, i, 852); when acted on by concentrated sulphuric acid, it yields *l-menthoethylheptanonolide*, crystallising in rectangular plates, m. p. 46–47°.

An attempt to prepare a pure active pinene by way of the crystalline *xanthate*, m. p. 36–37°, derived from *l-pinocampheol* (compare Tschugaeff, Abstr., 1908, i, 93), led to the production of a mixture of pinene and a dicyclic *terpene*; the latter, when oxidised, gave a crystalline dicarboxylic acid, $C_{10}H_{16}O_4$, m. p. 192–193°.

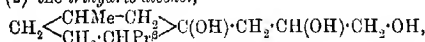
W. H. G.

Constituents of Ethereal Oils. Tetrahydrosantalene, $C_{15}H_{28}$. FRIEDRICH W. SEMMLER (*Ber.*, 1910, 43, 445–448. Compare Abstr., 1907, i, 431, 433, 1062; 1908, i, 433).—*Santalene dihydrochloride*, $C_{15}H_{28}, 2HCl$, obtained by the addition of hydrogen chloride to santalene in methyl-alcoholic solution, has b. p. 140–142°/0.55 mm., D^{20}_D 1.076, and n_D 1.4976. When distilled under 10 mm. pressure, it decomposes to a certain extent, yielding hydrogen chloride, and, when boiled with alcoholic potassium hydroxide, yields β -santalene.

When the dihydrochloride is reduced with sodium and boiling ethyl alcohol, it yields a mixture of hydrocarbons boiling at 119–123°/9 mm. The unsaturated hydrocarbons may be removed from this mixture by treatment with ozone, when pure *tetrahydrosantalene*, $C_{15}H_{28}$, is obtained. It has b. p. 116–118°/9 mm., D^{20}_D 0.864, n_D 1.4676, and n_D +7°30' (100 mm. tube). The hydrocarbon must be dicyclic, as it has all the properties of a saturated compound; it is thus analogous to dihydroeksantalol and dihydroeksantalic acid.

J. J. S.

Action of Magnesium and Allyl Bromide on Menthone. P. RYSCHENKO (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1695–1698. Compare Javorsky, Abstr., 1909, i, 168).—1-Methyl-4-isopropyl-3-allyl-cyclohexan-3-ol, $CH_2<\begin{smallmatrix} CHMe-CH_2 \\ CH_2-CHPr^{\beta} \end{smallmatrix}>C(CH_2\cdot CH\cdot CH_2)\cdot OH$, obtained on decomposing by means of water the Grignard compound yielded by magnesium, allyl bromide, and menthone, is a mobile, colourless liquid, b. p. 130–131°/22 mm., D^{20}_D 0.9028, n_D 1.470035, with an odour like that of mint. On oxidation with permanganate, it yields (1) menthol-acetic acid, $CH_2<\begin{smallmatrix} CHMe-CH_2 \\ CH_2-CHPr^{\beta} \end{smallmatrix}>C(CH_2\cdot CO_2H)\cdot OH$, which, when heated with potassium hydrogen sulphate, loses water and gives an acid, $C_{12}H_{20}O_2$; both of these acids were obtained by Wallach (Abstr., 1902, i, 799); (2) the *trihydric alcohol*,



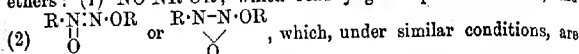
which is a pale yellow, syrupy, odourless liquid.

T. H. P.

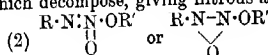
VOL. XXVIII. i.

o

Behaviour of Alicyclic Hydroxylamines and Hydroxylamineoximes towards Nitrous Acid. I. GUIDO CUSMANO (*Gazzetta*, 1909, 39, ii, 453—467. Compare Francesconi and Cusmano, *Abstr.*, 1909, i, 723, 724).—*iso*Nitroamines form two classes of ethers: (1) $\text{NO}\cdot\text{NR}\cdot\text{OR}'$, which readily give up nitrous acid, and

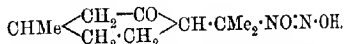
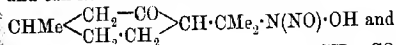


either stable or else yield nitrous oxide. Analogous behaviour is shown by the two classes of ether formed by the nitroamines, namely, (1) $\text{NO}_2\cdot\text{NRR}'$, which decompose, giving nitrous acid, and

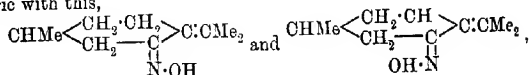


which yield nitrous oxide. It seems, then, that in these ethers the complex $-\text{N}_2\text{O}_2-$ can be completely eliminated from the forms $\begin{array}{c} \text{N}\cdot\text{N}\cdot\text{O}- \\ \parallel \\ \text{O} \end{array}$, $\begin{array}{c} \text{N}\cdot\text{N}\cdot\text{O}\cdot \\ \parallel \\ \text{O} \end{array}$, and $\begin{array}{c} \text{N}\cdot\text{N}\cdot\text{O}\cdot \\ \diagup \quad \diagdown \\ \text{O} \end{array}$, but not from the forms $-\text{N}(\text{NO}_2)-$

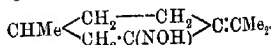
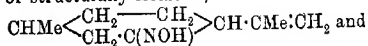
and $-\text{N}(\text{NO})\cdot\text{O}-$. Hence the nitroamines and isonitroamines, which in the free state probably possess the forms $\text{R}\cdot\text{NH}\cdot\text{NO}_2$ and $\text{R}\cdot\text{N}(\text{OH})\cdot\text{NO}$ respectively, retain these forms when they decompose with elimination of nitrous acid, but assume the forms $\text{R}\cdot\text{N}\cdot\text{NO}\cdot\text{OH}$ and $\text{R}\cdot\text{NO}\cdot\text{N}\cdot\text{OH}$ when decomposition is accompanied by separation of hyponitrous acid or nitrous oxide and water. As a rule, the known isonitroamines exhibit one or other of the above two methods of decomposition, but the author finds that, by varying the conditions, pulegonenitrosohydroxylamine (menthoisonitroamine) can be decomposed in both ways, and can hence react in the two forms:



By the action of hydroxylamine on pulegone, three compounds have been obtained: pulegonehydroxylamine, m. p. 154° (compare Beckmann and Pleissner, *Abstr.*, 1891, 936), an oxime, m. p. 120° (compare Wallach, *Abstr.*, 1896, i, 309), and $[\alpha]$ pulegonehydroxylamineoxime, m. p. 118° (compare Semmler, *Abstr.*, 1905, i, 222). The author has obtained two new derivatives of pulegone, namely, an oxime, m. p. 98°, and a $[\beta]$ hydroxylamineoxime, m. p. 143°. Wallach (*Terpene und Campher*, Leipzig, 1909) regards the oxime m. p. 120° as an oxime of *isopulegone*, and the oxime m. p. 98° is either stereoisomeric with this,

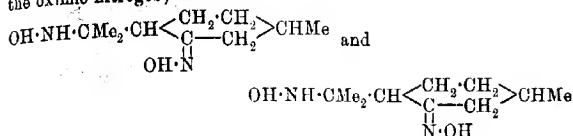


or structurally isomeric,

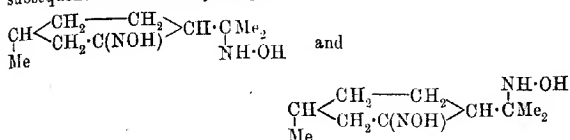


The new hydroxylamineoxime, m. p. 143°, is stereoisomeric with that

described by Semmler (*loc. cit.*), such isomerism being due either to the oximic nitrogen, thus :



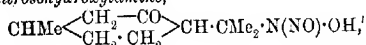
or to the method of rupture of the double linking of pulegone and the subsequent addition of hydroxylamine, thus :



Pulegoneoxime, $\text{C}_{10}\text{H}_{16}\text{:NOH}$, m. p. 98° , prepared by the action of hydrochloric acid on *isopulegoneoxime*, m. p. 120° , forms groups of laminae with triangular sections, reduces Fehling's solution, and is rapidly decomposed by heating with dilute sulphuric acid, but is not affected by boiling with alcoholic potassium hydroxide.

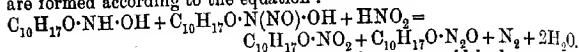
β -*Pulegonehydroxylamineoxime*, $\text{C}_{10}\text{H}_{20}\text{O}_2\text{N}_2$, which is obtained together with the α -isomeride and *isopulegoneoxime* when pulegone and hydroxylamine react under certain conditions, forms shining needles, m. p. 143° , reduces Fehling's solution instantaneously in the cold, and, when dissolved in organic solvents, is oxidised by the air to nitroso-compounds of a blue colour.

Pulegonenitrosohydroxylamine,

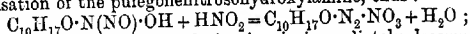


prepared by the action of nitrous acid on *pulegonehydroxylamine*, forms irregular, hexagonal crystals, m. p. 35° (decomp.), gives Liebermann's and the diphenylamine reactions, and in ethereal or alcoholic solution gives a garnet-red coloration with ferric chloride; it does not reduce Fehling's solution, but forms a *semicarbazone*, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{C}_{10}\text{H}_{17}\cdot\text{N}(\text{NO})\cdot\text{OH}$, m. p. 165° (decomp.), which gives Liebermann's and the diphenylamine reactions and a red coloration with ferric chloride. With hydroxylamine in alcoholic solution, *pulegonenitrosohydroxylamine* gives a white, hygroscopic substance, decomp. at 200° , which reduces Fehling's solution in the cold and gives Liebermann's reaction, but gives no coloration with ferric chloride. When suspended in water or dissolved in organic solvents, *pulegonenitrosohydroxylamine* is moderately stable, but in the dry state in the air, or in a vacuum, it undergoes rapid decomposition, yielding (1) *pulegone* and (2) 8-nitromenthone (compare Harries and Roeder, *Abstr.*, 1900, i, 182), which results from the oxidation of the 8-nitrosomenthone formed initially by the action of the air and of the nitric acid eliminated. With nitrous acid, *pulegonenitrosohydroxylamine* gives

pulegone and nitro- and nitroso-menthones. The last two compounds are formed according to the equation :



The formation of pulegone by the action of nitrous acid is due to the diazotisation of the pulegonenitrosohydroxylamine, thus :



the resulting aliphatic diazo-derivative is immediately decomposed by water into nitrogen, nitric acid, and 8-hydroxymenthone, the last compound then losing water and giving pulegone. When, however, decomposition of pulegonenitrosohydroxylamine occurs in presence of an alkali, it proceeds entirely in the one direction, the resultant products being pulegone and nitrous oxide: $\text{C}_{10}\text{H}_{17}\text{O}\cdot\text{NO}\cdot\text{N}\cdot\text{OH} + \text{H}_2\text{O} = \text{C}_{10}\text{H}_{17}\text{O}\cdot\text{OH} + \text{H}_2\text{O} + \text{N}_2\text{O}$ and $\text{C}_{10}\text{H}_{17}\text{O}\cdot\text{OH} = \text{C}_{10}\text{H}_{16}\text{O} + \text{H}_2\text{O}$.

T. H. P.

New Occurrence of *l*-Camphor. THEODOR WHITTLESSEY (*Festschrift Otto Wallach*, 1909, 668—670).—The oil obtained from a variety of "sage-brush" common to western North America, probably *Artemisia cana*, was found to have the following constants: D_{15}^{20} 0.9405; n_D^{20} 1.4702; acid number, 4.2, 4.1; ester number, 18.5, 19.8; saponification number, 22.7, 23.9; saponification number after acetylation, 111.8, 110.3. It contains *l*-camphor to the extent of at least 44.5%, an observation not without interest, for, with the exception observed by Wallach in the case of the broad-leaved *Salvia*, *l*-camphor has been found only in plants of the family *Compositae*.

W. H. G.

Coriander Oil. HEINRICH WALBAUM and WILHELM MÜLLER (*Festschrift Otto Wallach*, 1909, 654—667).—The sample of coriander oil examined had the following constants: D_{15}^{20} 0.8735; n_D^{20} 1.46387; acid number, 0; ester number, 20.22; ester number after acetylation, 159, corresponding with 49.65% of linalool; it is possible to obtain, however, 70% of the latter substance by fractional distillation on a large scale. Roughly, 20% of the oil consists of almost equal quantities of α -d-pinene, *p*-cymene, and terpinenes (α - and γ -terpinene), together with very small quantities of β -pinene, dipentene, and possibly, also, phellandrene and terpinolene. The presence of decylaldehyde, geraniol, *l*-borneol, and esters of these, alcohols was also established. In addition to the compounds mentioned, coriander oil contains small quantities of unknown substances, which are of importance in imparting aroma to the oil.

W. H. G.

[Essential Oils.] ROURE-BERTRAND FILS (*Sci. Ind. Bull. Roure-Bertrand Fils*, 1909, [ii], 10, 19—43).—This contains the following new work:

[JUSTIN DUPONT and LOUIS LABAUNE].—*Action of Hydrochloric Acid on Linalool and Geraniol* (compare Grosser, Abstr., 1882, 525; Barbier, *ibid.*, 1892, 1236; 1895, i, 78).—When dissolved in toluene and treated with gaseous hydrogen chloride at 100°, both alcohols yield *linalyl chloride*, $\text{C}_{10}\text{H}_{17}\text{Cl}$, D_{15}^{20} 0.9341, $[\alpha]_D^{20}$ 1.50°, n_D^{20} 1.4813, and b. p. 95—96°/6 mm. This on treatment with silver nitrate in alcohol

regenerates linalool. The chloride obtained from geraniol could not be obtained quite pure. At -4° to $+3^{\circ}$ the action of hydrogen chloride on linalool or geraniol in toluene is more complicated. No water is formed until the mixture regains atmospheric temperature. The product formed is a mixture of linalyl chloride with a dichloro-derivative. Cinnamyl alcohol at 100° yields a chloride, C_9H_9Cl , D^{20}_4 1.0857, n_D^{20} 1.583, b. p. $115-116^{\circ}/6$ mm., which absorbs bromine, forming a dibromide, m. p. 104° , and on treatment with silver nitrate in alcohol yields a mixture of two alcohols, one of which may be phenylallyl alcohol (Klages and Klenk, Abstr., 1906, i, 638).

[J. LEROIDE].—*Preparation of Fenchone free from Camphor*.—The best results were obtained by warming crude fenchone with aluminium chloride and then distilling under reduced pressure. For the detection of camphor the semicarbazide test was employed, which is sufficient to show the presence of 0.1% of camphor. By this means camphor was proved to occur naturally in fennel oil. Thujone cannot be eliminated from mixtures of this ketone with camphor and fenchone by treatment with aluminium chloride and bromine, and in such cases oxidation with nitric acid must be resorted to, the camphor being subsequently removed by treatment with aluminium chloride and bromine.

Four oils from the Comores Islands were examined, and gave the following results: Bigarade oil had D^{15}_D 0.8812, $\alpha_D + 42^{\circ}13'$, and was insoluble in 80% alcohol.

Petitgrain oil had D^{15}_D 0.8650, $\alpha_D + 42^{\circ}18'$, and saponification value 33.6.

Basil oil had D^{15}_D 0.9588, $\alpha_D 0^{\circ}35'$, and saponification value 4.2.

Citronella oil had D^{15}_D 0.8922, $\alpha_D - 0^{\circ}52'$, aldehydes 80% (by bisulphite process), and was insoluble even in absolute alcohol.

Ylang-ylang oil, from Nossi-Bé, had D^{15}_D 0.9673, $\alpha_D - 42^{\circ}12'$, acid value 1.4, saponification value 129.5, esters 45.3%, and total alcohols 42.7%.

Linalce oil, from Cayenne, had D^{20}_D 0.8721, $\alpha_D - 12^{\circ}56'$, n_D^{20} 1.4635, and contained methylheptenone, *d*-terpineol, geraniol, *l*-linalool, and nerol (?).

T. A. H

Constituents of Oil of Lemon. EDUARD GILDENEISTER and WILHELM MÜLLER (*Festschrift Otto Wallach*, 1909, 439—451).—Oil of lemon contains in addition to *l*-limonene a moderate quantity of *l*- β -pinene, and very small quantities of α -pinene, *i*- α -pinene, *l*-camphene, β -phellandrene, and γ -terpinene. The sesquiterpene obtained from the oil in small quantity (compare Burgess and Page, Trans., 1904, 85, 414) is shown to be identical with bisabolene (compare Tscholka, Abstr., 1897, ii, 584); the same hydrocarbon is present in opoponax oil, oil of *Piper Volkensii* (compare Schmidt and Weillinger, Abstr., 1906, i, 299), and camphor oil.

The erythritol from γ -terpinene (compare Wallach, Abstr., 1908, i, 811) undergoes the following changes: (1) when boiled with acids it yields a mixture of thymol and carvacrol; (2) it yields a brominated substance, crystallising in large leaflets, m. p. $93-94^{\circ}$, when treated with an alkaline solution of hypobromite; (3) when oxidised with an

alkaline solution of potassium permanganate it yields oxalic acid and an acid, m. p. 147—149°, which is probably isopropyltartronic acid.

W. H. G.

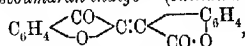
Essential Oil from the Seeds of *Monodora grandiflora*. ROBERT LEIMBACH (*Festschrift Otto Wallach*, 1909, 502—512).—The oil obtained by the steam distillation of the seeds of *Monodora grandiflora* is a limpid, pale yellow oil, with an odour resembling cymene, D_{20}^{25} 0.8574, n_D^{25} 1.4625° in a 1-dm. tube, acid number 3.6, saponification number 7—12. Nearly 90% of the oil consists of hydrocarbons, chiefly *l*-phellandrene, camphene, and *p*-cymene. The remainder, a heavy oil with an aromatic odour, contains palmitic acid, carvacrol, a substance, $C_{16}H_{16}O$, which reacts neither as an alcohol nor a ketone, a sesquiterpene, $C_{15}H_{24}$, b. p. 260—270°, D_{20}^{25} 0.9138, n_D^{25} 1.50513, a crystalline substance, m. p. 160—163°, and small quantities of other unknown substances.

W. H. G.

A Condensation Product of Coumaranone and its Conversion into Oxindirubin. KARL FRIES and W. PFAFFENDORFF (*Ber.*, 1910, 43, 212—219).—The constitutions have been ascertained of the compound, $C_{18}H_{14}O_4$, obtained from 4-methyl-2-coumaranone or from ω -chloro-2-hydroxy-5-methylacetophenone (Abstr., 1909, i, 44), and also of those obtained by a similar process from 5-methyl-2-coumaranone or ω -chloro-2-hydroxy-4-methylacetophenone, and from 2-coumaranone or ω -chloro-2-hydroxyacetophenone. An ethereal solution of 2-coumaranone is treated with sodium and then with acetyl chloride, whereby the acetate, m. p. 106°, of 2-hydroxy-1:2'-dicoumarone, $C_6H_4 \begin{smallmatrix} \diagup C(OH) \diagdown \\ \diagdown O \diagup \end{smallmatrix} C \cdot C \begin{smallmatrix} \diagup C_6H_4 \diagdown \\ \diagdown CH \cdot O \diagup \end{smallmatrix}$, is formed; the parent substance has

not been obtained pure. By warming an alcoholic solution of the acetate with sodium ethoxide and subsequently acidifying, by boiling an acetic acid solution of the acetate with hydrogen peroxide, or by the prolonged heating of 2-coumaranone or ω -chloro-2-hydroxyacetophenone with alcoholic sodium ethoxide, 2:1'-*dihydroxy*-1:2'-dicoumarone (leuco-oxindirubin), $C_6H_4 \begin{smallmatrix} \diagup C(OH) \diagdown \\ \diagdown O \diagup \end{smallmatrix} C \cdot C \begin{smallmatrix} \diagup C_6H_4 \diagdown \\ \diagdown C(OH) \cdot O \diagup \end{smallmatrix}$, m. p. 185°,

is obtained, which forms orange-yellow needles, gives a deep red, non-fluorescent solution in concentrated sulphuric acid, and by the prolonged heating of its solution in glacial acetic acid, or, more readily, by treating the solution with hydrogen peroxide or bromine, is converted into "1:2'-*biscoumaran-indigo*" (oxindirubin),



m. p. 215°, which is also obtained by treating an acetic acid solution of 2-coumaranone and *o*-hydroxybenzoyl formic acid with concentrated sulphuric acid.

By a similar series of reactions, 5-methyl-2-coumaranone yields the acetate, m. p. 133°, of 2-hydroxy-5:5'-dimethyl-1:2'-dicoumarone, 2:1'-*dihydroxy*-5:5'-dimethyl-1:2'-dicoumarone (5:5'-dimethyl-leuco-oxindirubin), m. p. 204°, and "1:2'-bis(5-methylcoumaran)-indigo"

(5:5'-dimethyloxindirubin). The compound $C_{13}H_{14}O_4$ (*loc. cit.*) is 4:4'-dimethyl-leuco-oxindirubin.

Oxonium Perchlorates. KARL A. HOFMANN, A. METZLER, and H. LECHER (*Ber.*, 1910, 43, 178—183. Compare Abstr., 1909, ii, 568).—Seventy per cent. perchloric acid yields crystalline compounds with ketones, and similar substances with basic properties; these are sparingly soluble and admirably adapted for characterising and isolating ketones. Even substances, such as carbazole, in which the basic properties of the nitrogen are very feeble, form crystalline salts. The perchlorates afford a better test of basic properties than picrates. These salts are regarded as oxonium derivatives.

A solution of xanthone in tetrachloroethane gives a bright yellow precipitate of *xanthone perchlorate*, $C_{13}H_8O_5 \cdot HClO_4$, which can be recrystallised from tetrachloroethane without decomposition, but is very rapidly decomposed by traces of moisture.

Carbazole perchlorate crystallises in lustrous, colourless plates; it is decomposed by water. Prolonged action with an excess of perchloric acid leads to the formation of a greenish-blue compound.

A colourless perchlorate is also formed by quinone di-imide. This explodes on heating. When moistened with water, it becomes a brilliant bluish-green, then violet, and then brown.

Benzophenone forms a yellow solution and a bright brownish-yellow, crystalline mass. This rapidly decomposes in moist air, leaving colourless oily drops, which do not crystallise until inoculated with a crystal of benzophenone. The perchlorate is apparently derived from the allotropic low melting variety of benzophenone.

Anthraquinone and alizarin do not react with perchloric acid. *Phenanthraquinone perchlorate* forms a mass of blood-red crystals in solution, which dry to red needles, but rapidly become bright orange when exposed to moist air. The *hemiperchlorate*, $(C_{14}H_8O_2)_2 \cdot HClO_4$, is obtained in flat, obliquely-cut, yellow or brownish-red prisms.

From retenequinone only the *hemiperchlorate* has been isolated. *Naphthazarin perchlorate* forms large, rectangular, stout plates with a bronze lustre.

E. F. A.

New Selenium Compound. IDA FOA (*Gazzetta*, 1909, 39, ii, 527—534).—*Selenophen*, $\begin{matrix} \text{CH:CH} \\ \text{CH:CH} \end{matrix} \text{Se}$, obtained by heating sodium succinate with phosphorus triselenide, is a yellow, mobile, irritant liquid, b. p. 147—149°/250 mm.; it dissolves in concentrated sulphuric acid, giving a reddish-brown coloration, whilst with a solution of isatin in concentrated sulphuric acid, a dark carmine coloration is obtained. In presence of acetic acid, it forms with bromine an unstable, liquid bromide.

T. H. P.

Production of a Volatile Aromatic Substance from Solutions of Morphine Salts. C. REICHARD (*Pharm. Zentr.-h.*, 1910, 51, 128—130).—When a solution of morphine hydrochloride or sulphate in water is heated, a slight odour of musk is developed, and the

strength of this odour increases with the concentration of the alkaloidal solution, and with the quantity of water vapour produced from the solution.

T. A. H.

Partial Racemism. H. DETILH (*Proc. K. Akad. Wetensch. Amsterd.*, 1909, 12, 393—400).—The author has studied the partial racemism which occurs with strychnine racemate, more especially by observing the behaviour of this compound in presence of its aqueous solution. The investigation was carried out on the lines indicated by Roozeboom (*Abstr.*, 1899, ii, 401), who pointed out the probable inaccuracy of the results obtained by Ladenburg and Doctor (*Abstr.*, 1899, i, 310). By means of the solubility curves of the *d*, *l*, *l+r*, and *d+r*-compounds at 40°, 25°, 16°, and 7·5°, it was found that the transition interval, which Ladenburg and Doctor assumed to be non-existent, extended over about 20°. Saturated solutions of the partial racemate are stable only below 7·5°, although the solubility at higher temperatures can be determined by retarding the decomposition.

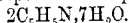
The author has avoided determining by means of the polarimeter the content of the *l*- and *d*-compounds in liquids saturated with the *r+d*-, *r+l*-, or *d+l*-compounds, and suggests that such method of analysis gives a wrong idea concerning the inner composition of a solution saturated with two salts. This view is supported by the results obtained by Findlay and Hickmans (*Trans.*, 1909, 95, 1386), who, using the polarimetric method of estimation, found that the addition of *l*-menthyl *l*-mandelate diminishes the solubility of *l*-menthyl *d*-mandelate at 10°, whilst it increases it at 25° or 35°; such behaviour the author regards as improbable.

T. H. P.

Hæmopyrrole. LEON MARCHLEWSKI (*Ber.*, 1910, 43, 259—260).—Polemical. A reply to Piloty (this vol., i, 133).

R. V. S.

Pyridine Hydrate. WILLIAM OECHSNER DE CONINCK (*Bull. Soc. chim. Belg.*, 1910, 24, 55).—From basic tar oils the author has isolated a product which has the composition of a pyridine hydrate,



This has b. p. 91—93°, but it is not regarded as a definite chemical compound (compare Goldschmidt and Constam, *Abstr.*, 1884, 611).

T. A. H.

Condensation of Esters of Acetonedicarboxylic Acid with Aldehydes by means of Ammonia and Amines. VI Tautomerism of Ethyl 2:6-Diphenyl-4-pyridone-3:5-dicarboxylate. PAVEL IW. PETRENKO-KRITSCHENKO and JOH. SCHÖTTIG (*Ber.*, 1910, 43, 203—206).—The methylation of ethyl 2:6-diphenyl-4-pyridone-3:5-dicarboxylate in alkaline solution leads to the formation of 2:6-diphenyl-1-methyl-4-pyridone-3:5-dicarboxylic acid, m. p. 270°, and a mixture, m. p. 125—130° (*Abstr.*, 1909, i, 605). By hydrolysing the latter by 7% aqueous alkali and subsequent acidification, a *acid*, $C_{20}H_{15}O_5N$, is obtained, which separates from dilute acetic acid in crystals, m. p. 240° (decomp.), containing $1\frac{1}{2}C_2H_4O_2$, and forms a *ethyl ester*, m. p. 229—230°, which is insoluble in ammonium

hydroxide. The acid is probably 4-methoxy-3:6-diphenylpyridine 3:5-dicarboxylic acid. C. S.

Anthranil. XVI. Relation of Anthroxanic Acid (2-Anthranilcarboxylic Acid) to Anthranil. EUGEN BAMBERGER and SVEN LINDBERG (*Ber.*, 1910, 43, 122—127. Compare *Abstr.*, 1909, i, 509, 510, 511).—*o*-Amino- and *o*-nitro-aromatic aldehydes and ketones are converted by mild oxidising and reducing agents respectively into anthranil derivatives. To establish the constitution of anthroxanic acid as anthranil-2-carboxylic acid, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \text{---} \text{O} \\ | \quad \diagup \\ \text{C}(\text{CO}_2\text{H}) \end{smallmatrix}$, the behaviour of isatinic acid and *o*-nitrophenylglyoxylic acid has been studied.

By the oxidation of isatinic acid with Caro's reagent, anthroxanic acid, 2:2'-azoxybenzoic acid, and *o*-nitrosobenzoic acid are formed. The last product affords strong support to the view that *o*-hydroxylaminophenylglyoxylic acid, $\text{OH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}_2\text{H}$, is the first intermediate oxidation product.

o-Nitrophenylglyoxylic acid, when reduced by tin and acetic acid, forms anthroxanic acid and a compound, m. p. 127°, probably 1-acetyl-dioxindole, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}(\text{OH}) \\ | \quad \diagup \\ \text{N}(\text{CO}\cdot\text{CH}_3) \end{smallmatrix} \text{CO}$. E. F. A.

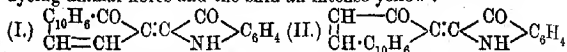
Cinchonic Acid Syntheses. WALTHER BORSCHÉ (*Ber.*, 1910, 43, 267).—A reply to Schiff (this vol., i, 131). R. V. S.

Elimination of Alkyl Radicles and Fission of Organic Bases by means of Cyanogen Bromide and Phosphorus Halides. JULIUS VON BRAUN (*Festschrift Otto Wallach*, 1909, 313—386).—A résumé of the author's investigations on this subject (compare *Abstr.*, 1904, i, 688, 731, 841, 918; 1905, i, 596, 634, 636, 826; 1906, i, 576; 1907, i, 28, 79, 105, 110, 127, 151, 524, 728, 899, 960; 1908, i, 625, 627, 675, and 685). The following observations have not been recorded previously. Quinoline is converted by cyanogen bromide and water into a crystalline substance, m. p. 113°, which probably has the formula $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}=\text{CH} \\ | \quad | \\ \text{N}(\text{CN}) \quad \text{CH}\cdot\text{OH} \end{smallmatrix}$.

Benzoylbexahydrocarbazole and the 4-methyl compound (compare Borsche, *Abstr.*, 1908, i, 365), when acted on by phosphorus chlorides, yield 2-benzoylaminodiphenyl, m. p. 102°, and 2'-benzoylamino-4-methyldiphenyl, m. p. 121°, respectively. W. H. G.

Indigoid Dyes. V. Indigoid Dyes of the Anthracene Series. A. BEZDIK and PAUL FRIEDLÄNDER (*Monatsh.*, 1909, 30, 871—878. Compare *Abstr.*, 1909, i, 415, 417).—Isatin chloride and isatinanilide condense with hydroxy-derivatives of anthracene, forming indigoid dyes, which are far more stable towards acids and alkalis than the analogous naphthalene compounds (compare *Abstr.*, 1908, i, 673); for example, 1-keto-2-indoxylantracene is not decomposed by sodium hydroxide, although the isomeride, 2-keto-1-indoxylantracene, when similarly treated yields anthranilic acid and 2-hydroxy-

1-anthracenealdehyde. The latter substance has the property of dyeing animal fibres and the skin an intense yellow:



1-*Keto-2-indoxylanthracene* (I), prepared by the condensation of α -anthrol and isatinanilide in acetic anhydride, crystallises in small, dark blue needles with a bronzy reflex, melts and sublimes with decomposition at a high temperature, and, when reduced with an alkaline solution of hyposulphite, yields an orange-red solution which dyes textile fibres a pure blue.

2-*Keto-1-indoxylanthracene* (II), similarly prepared from β -anthrol, forms small, dark blue needles with a coppery reflex, and sublimes with decomposition at a high temperature. 2-*Hydroxy-1-anthracenealdehyde*, $\text{C}_{16}\text{H}_{10}\text{O}_2$, crystallises in long, pale yellow needles, m. p. 164° ; the *oxime* crystallises in four-sided, pale green plates, m. p. 197° (decomp.); the *phenylhydrazone* forms flat, yellow prisms, m. p. $224-225^\circ$; the *aldazine* forms slender, brick-red needles, m. p. above 300° .

5-*Hydroxy-1-keto-2-indoxylanthracene*, $\text{C}_{22}\text{H}_{18}\text{O}_5\text{N}$, prepared from 1:5-dihydroxyanthracene and isatin chloride, crystallises in long, slender, dark blue needles; the isomeric 8-*hydroxy*-compound is very similar in properties, but is slightly more green. W. H. G.

Synthesis of Oxazoles and Thiazoles. I. SIEGMUND GABRIEL (*Ber.*, 1910, 43, 134—138).—By the action of phosphorus pentachloride on benzoylaminoacetophenone, 4-*chloro-2:5-diphenyloxazole* is formed, and not a chlorinated *isoquinoline* derivative, as might be expected from analogy to the synthesis of dihydroisoquinolines from acyl derivatives of phenylethylamine.

ω -Benzoylaminoacetophenone is best prepared from ω -aminoacetophenone hydrochloride by the action of benzoyl chloride in acetic acid solution; it has m. p. 124° [Robinson, *Trans.*, 1909, 95, 2169, gives 123°]. When heated with two mols. of phosphorus pentachloride, first at the temperature of the water-bath and later to 170° , 4-*chloro-*

2:5-*diphenyloxazole*, $\text{O} < \begin{array}{c} \text{CPh}\cdot\text{CCl} \\ \text{CPh}\cdot\text{N} \end{array}$, is formed, crystallising in slender needles, m. p. $67-68^\circ$. When heated with sodium amalgam in

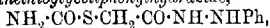
alcoholic solution, 2:5-*diphenyloxazole*, $\text{O} < \begin{array}{c} \text{CPh}\cdot\text{CH} \\ \text{CPh}\cdot\text{N} \end{array}$, is obtained (compare E. Fischer, *Abstr.*, 1896, i, 262). The same compound may be obtained in one operation from benzoylaminoacetophenone when only one molecule of phosphorus pentachloride is used. Similarly, when benzoylaminoacetophenone and phosphorus pentasulphide are heated at

170° , 2:5-*diphenylthiazole*, $\text{S} < \begin{array}{c} \text{CPh}\cdot\text{CH} \\ \text{CPh}\cdot\text{N} \end{array}$, is formed, crystallising in large, rhombic plates, m. p. $103-104^\circ$. E. F. A.

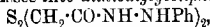
Action of Hydrazines on Thiocyanacetic Acid and its Ethyl Ester. GUSTAV FRERICHs and PAUL FÖRSTER (*Annalen*, 1910, 371, 227—257).—The nature of the interaction of thiocyanacetic acid and phenylhydrazine as described by Harries and Klamt (*Abstr.*,

1900, i, 413) not being strictly analogous to that of thiocyanacetic acid and aniline (compare Rizzo, Abstr., 1898, i, 659; Beckurts and Frerichs, Abstr., 1902, i, 763), it was deemed advisable to repeat the work of the first-named investigators, the outcome of which has been the direct negation of many of the statements of these authors.

When phenylhydrazine is added to a cold ethereal solution of thiocyanacetic acid, a white, crystalline precipitate of *phenylhydrazine thiocarbimidoacetate*, $\text{SCN}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}\cdot\text{NH}_2\cdot\text{N}\cdot\text{Ph}$, m. p. 92—100°, is obtained, which, when kept for some time, or when boiled with alcohol, passes into *carbamimethioglycollphenylhydrazide*,

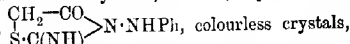


colourless leaflets, m. p. 149°. The latter substance is more readily obtained by the interaction of phenylhydrazine, chloroacetic acid, and potassium thiocyanate in alcoholic solution; when heated at about 155° for an hour, it passes into *dithiodiglycollphenylhydrazide*,

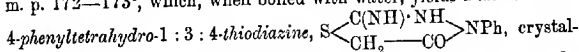


which crystallises in colourless, glistening leaflets, m. p. 174°, and is also formed by heating carbaminethioglycollphenylhydrazide with 10% aqueous ammonia and treating the solution subsequently with hydrogen peroxide.

When ethyl thiocyanacetate is boiled with an alcoholic solution of phenylhydrazine, it yields ammonium cyanate, a viscid, oily substance, and 3-*anilinothiohydantoin*,

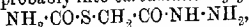


m. p. 176°, which dissolve in concentrated sulphuric acid and aqueous potassium hydroxide, forming blue and violet solutions respectively; the substance just described is also formed by the action of phenylthiosemicarbazine on chloroacetic acid. The interaction of chloroacetylphenylsemicarbazine and potassium thiocyanate in alcoholic solution leads to the formation of *thiocarbimidoacetylphenylsemicarbazine*, $\text{SCN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, small, glistening crystals, m. p. 172—173°, which, when boiled with water, yields 2-*imino-5-keto-4-phenyltetrahydro-1:3:4-thiadiazine*,

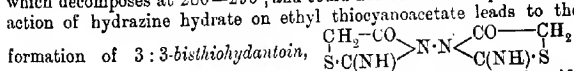


lising in pale yellow needles, m. p. 161—162°; the crystalline salts with the halogen acids, $\text{C}_6\text{H}_5\text{ON}_3\text{S}_2\text{HX}$, were prepared.

Hydrazine hydrate and thiocyanacetic acid combine, yielding *hydrazine thiocarbimidoacetate*, $\text{SCN}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}\cdot\text{N}_2\text{H}_4$, glistening leaflets, m. p. 87—90°, which undergoes intermolecular rearrangement when kept, passing probably into *carbamimethioglycollhydrazide*,



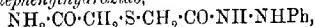
m. p. about 125°, and, when boiled with water, yields a substance, which decomposes at 280—290°, and could not be obtained pure. The action of hydrazine hydrate on ethyl thiocyanacetate leads to the



the same substance is formed by the interaction of bisthiocarbamide (hydrazodicarboxythioamide) and chloroacetic acid; it decomposes without melting at a high temperature.

Carbamimethioglycollphenylhydrazide undergoes the following

changes: (1) when boiled with 10% aqueous ammonia and subsequently treated with hydrochloric acid, it yields *thioglycollphenylhydrazide*, $\text{NHPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SH}$, leaflets, m. p. 112—113°; (2) it is converted by alcoholic potassium hydroxide and methyl iodide under pressure at 100° into *methylthioglycollphenylhydrazide*, $\text{C}_6\text{H}_5\text{ON}_2\text{S}$, glistening leaflets, m. p. 104—105°; the corresponding *ethyl* compound, $\text{C}_{10}\text{H}_{14}\text{ON}_2\text{S}$, forms colourless leaflets, m. p. 84—85°; (3) when heated with alcoholic potassium hydroxide and chloroacetamide, it yields *thiodiglycollamidophenylhydrazide*,



colourless leaflets, m. p. 135—136°; (4) with alcoholic potassium hydroxide and ethyl chlorocarbonate it yields *carboxythioglycollphenylhydrazide*, $\text{CO}_2\text{H}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NHPh}$, m. p. 156—157°; the *potassium* salt has m. p. 212—213°.

The following substances are prepared by methods similar to those just described: *phenylmethylhydrazinethiocyanacetate*, m. p. 65—68°; *carbamimethioglycollphenylmethylhydrazide*, $\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}_2\text{S}$, m. p. 145—146°; *methylthioglycollphenylmethylhydrazide*, $\text{C}_{10}\text{H}_{14}\text{ON}_2\text{S}$, needles, m. p. 74—75°; *carbethoxythioglycollphenylmethylhydrazide*, $\text{C}_{12}\text{H}_{16}\text{O}_3\text{N}_2\text{S}$, colourless leaflets, m. p. 82—83°; *carbamimethioglycoll-p-tolylhydrazide*, $\text{C}_{16}\text{H}_{19}\text{O}_2\text{N}_2\text{S}$, m. p. 164—165°; *thioglycoll-p-tolylhydrazide*, $\text{C}_9\text{H}_{13}\text{ON}_2\text{S}$, m. p. 125—126°; *dithiodiglycoll-p-tolylhydrazide*, $\text{C}_{18}\text{H}_{21}\text{O}_2\text{N}_2\text{S}_2$, glistening leaflets, m. p. 182—183°; *methylthioglycoll-p-tolylhydrazide*, $\text{C}_{10}\text{H}_{14}\text{ON}_2\text{S}$, glistening leaflets, m. p. 108—109°; *thiodiglycollamide-p-tolylhydrazide*, $\text{C}_{11}\text{H}_{15}\text{O}_2\text{N}_2\text{S}$, glistening, pale yellow needles, m. p. 148—149°.

W. H. G.

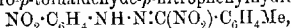
Case of Isomerism. [Acylazoaryl Compounds.] GIACOMO PONZIO (*Gazzetta*, 1909, 39, ii, 535—546).—The author has carried out further investigations on the yellow, white, and red isomerides, $\text{C}_{15}\text{H}_{10}\text{O}_4\text{N}_4$, obtained by the action of benzenediazonium acetate on the potassium derivative of ω -dinitrotoluene (Abstr., 1908, i, 482, 582; 1909, i, 443, 681). The results obtained settle definitely the structure of the red isomeride, and render probable the accuracy of that already assigned to the white compound, but do not admit of the structure of the yellow derivative being determined.

For the yellow compound, the author has suggested the formula $\text{NO}_2\cdot\text{CPh}(\text{NO})\cdot\text{O}\cdot\text{N}\cdot\text{NPh}$, which would explain its isomeric change into α -nitro- β -nitroso- α -benzoyl- β -phenylhydrazine (Abstr., 1908, i, 482). On the basis of this formula, Dimroth and Hartmann (Abstr., 1909, i, 66) indicate an analogy between this yellow compound and benzene-*O*-azotribenzoylmethane, obtained by the interaction of the potassium derivative of tribenzoylmethane with benzenediazonium acetate, and suggest that the yellow compound is a true *O*-azo-derivative and not a diazo-derivative. But, apart from the fact that the properties of Dimroth and Hartmann's compound are explained equally well by regarding it as a true diazonium salt (compare Auwers, Abstr., 1909, i, 67), its analogy to the author's yellow compound is not borne out by its behaviour with ethereal hydrochloric acid. Thus, benzene-*O*-azotribenzoylmethane gives benzene-diazonium chloride and tribenzoylmethane, whilst the diazobenzene

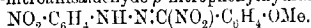
derivative of ω -dinitrotoluene gives the isomeric compounds, α -nitro- β -nitroso- α -benzoyl- β -phenylhydrazine and ω -nitrobenzaldehyde- p -nitrophenylhydrazone, $\text{NO}_2\cdot\text{CPh}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, treatment with water converting the former of these isomerides into β -nitroso- α -benzoyl- β -phenylhydrazine and leaving the latter unchanged. The formula $\text{NO}_2\cdot\text{CPh}(\text{NO})\cdot\text{N}\cdot\text{NPh}$ for the yellow compound (*vide supra*) does not, however, explain its reaction with alcohol, with formation of ω -dinitrotoluene, nitrogen, acetaldehyde, and benzene.

The reactions of the red isomeride are not in accord with the structure, $\text{NPh}\cdot\text{N}\cdot\text{CPh}(\text{NO}_2)_2$, originally assigned to it (Abstr., 1908, i, 482). Thus, on reduction by means of tin and hydrochloric acid, it yields ammonia, benzoic acid, and p -phenylenediamine. By sodium methoxide it is converted into α -dinitrotetraphenyltetrazoline (compare Bamberger and Grob, Abstr., 1901, i, 296). These results indicate that the red compound is not ω -benzeneazo- ω -dinitrotoluene, but ω -nitrobenzaldehyde- p -nitrophenylhydrazone (compare Bamberger and Grob, Abstr., 1901, i, 567), and direct comparison confirms this indication. The isomeric change of the yellow compound into ω -nitrobenzaldehyde- p -nitrophenylhydrazone consists in the passage of a nitro-group from an aliphatic carbon atom into the para-position of the benzene nucleus, and such a transformation is best explained by regarding the yellow compound as ω -benzeneazo- ω -dinitrotoluene, $\text{NPh}\cdot\text{N}\cdot\text{CPh}(\text{NO}_2)_2$.

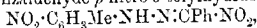
It follows from these results that the compound, m. p. 130—135°, previously described as ω -dinitro- ω -benzeneazo- p -xylene, must be regarded as ω -nitro- p -tolualdehyde- p -nitrophenylhydrazone,



and that described as ω -dinitro- ω -benzeneazo- p -methoxytoluene, m. p. 141—148°, as ω -nitroanisaldehyde- p -nitrophenylhydrazone,

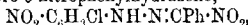


But, in addition to the diazobenzene derivatives of the primary dinitrohydrocarbons, the ortho-substituted diazo-salts are also transformed into red isomerides when dissolved in moist ether, and in this case, too, there takes place transference of a nitro-group from the aliphatic carbon atom to the para-position of the benzene nucleus. So that the compound, m. p. 137° (decomp.), previously described (Abstr., 1909, i, 443) as ω - ω -tolueneazo- ω -dinitrotoluene must be regarded as ω -nitrobenzaldehyde- p -nitro- o -tolylhydrazone,



a structure which is confirmed by the fact that it yields benzoic acid, ammonia, and 2:5-diaminotoluene on reduction with tin and hydrochloric acid; this compound may also be obtained by the interaction of the sodium derivative of ω -nitrotoluene and m -nitro- o -toluenediazonium sulphate: $\text{CHPh}\cdot\text{NO}_2\cdot\text{Na} + \text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{N}_2\cdot\text{HSO}_4 = \text{NaHSO}_4 + \text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}\cdot\text{N}\cdot\text{CPh}\cdot\text{NO}_2$. Further, the compounds described as ω - o -chlorobenzeneazo- ω -dinitrotoluene, m. p. 140° (decomp.), and ω - o -bromobenzeneazo- ω -dinitrotoluene, m. p. 140° (decomp.) (Abstr., 1909, i, 443), must be regarded as the o -chloro- p -nitrophenylhydrazone and o -bromo- p -nitrophenylhydrazone respectively of ω -nitrobenzaldehyde, $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{NH}\cdot\text{N}\cdot\text{CPh}\cdot\text{NO}_2$ and $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{NH}\cdot\text{N}\cdot\text{CPh}\cdot\text{NO}_2$.

These results explain the observation that, whilst the ortho-substituted diazonium salts give with moist ether their red isomerides, that is, the corresponding ortho-substituted *p*-nitrohydrazones, para-substituted diazonium salts, under the same conditions, lose two atoms of nitrogen and three of oxygen in the form of nitrous compounds, giving acylazoaryl derivatives, the isomeric acylarylnitronitrosohydrazines being formed as intermediate products: $R \cdot C(N_2O_2) \cdot N_2Ar \rightarrow R \cdot CO \cdot N(NO_2) \cdot NAr \cdot NO \rightarrow R \cdot CO \cdot N \cdot NAr$; the para-position which the nitro-group tends to assume is in these cases occupied. It is found, indeed, that these compounds, by the action of absolute alcohol in the cold, give small yields of red isomerides, the nitro-group entering the benzene nucleus in the ortho-position. The red isomeride, m. p. 153—154° (decomp.), of the *p*-diazotoluene derivative of *o*-dinitrotoluene (Abstr., 1909, i, 443) is found to be, not *o*-*p*-tolueneazo-*o*-dinitrotoluene, but *o*-nitrobenzaldehyde-*o*-nitro-*p*-tolylhydrazone, $NO_2 \cdot C_6H_4 \cdot Me \cdot NH \cdot N : CPh \cdot NO_2$; reduction of this compound (which may also be obtained by the interaction of the sodium derivative of *o*-nitrotoluene and *m*-nitro-*p*-toluenediazonium sulphate: $CHPh \cdot NO_2 \cdot Na + NO_2 \cdot C_6H_4 \cdot Me \cdot N_2 \cdot HSO_4 = NaHSO_4 + NO_2 \cdot C_6H_4 \cdot Me \cdot NH \cdot N : CPh \cdot NO_2$) with tin and hydrochloric acid gives benzoic acid, ammonia, and 3:4-diaminotoluene. Similarly, the compound described as *o*-*p*-chlorobenzeneazo-*o*-dinitrotoluene (Abstr., 1909, i, 443), m. p. 161° (decomp.), must be regarded as *o*-nitrobenzaldehyde-*p*-chloro-*o*-nitrophenylhydrazone,



and that described as *o*-*p*-bromobenzeneazo-*o*-dinitrotoluene as *o*-nitrobenzaldehyde-*p*-bromo-*o*-nitrophenylhydrazone,



That the white isomeride, best obtained by dissolving the diazobenzene derivative of *o*-dinitrotoluene in anhydrous benzene, is *o*-nitro-*β*-nitroso-*α*-benzoyl-*β*-phenylhydrazine, $NO_2 \cdot NBz \cdot NPh \cdot NO$, is confirmed by its transformation into benzoylazobenzene, $NBz \cdot NPh$ (Abstr., 1909, i, 681). T. H. P.

Passage of the Nitro-group from an Aliphatic Carbon Atom to the Benzene Nucleus. GIACOMO PONZIO and R. GIOVETTI (*Gazzetta*, 1909, 39, ii, 546—556).—The action of the sodium derivative of *o*-isonitrophenylacetonitrile on benzenediazonium acetate yields benzeneazo-*o*-nitrophenylacetonitrile, $NO_2 \cdot CPh(CN) \cdot N : NPh$, which, by the passage of the nitro-group to the para-position of the benzene nucleus, undergoes spontaneous transformation into *o*-cyanobenzaldehyde-*p*-nitrophenylhydrazone, $CN \cdot CPh : N \cdot H \cdot C_6H_4 \cdot NO_2$, and a small proportion of the corresponding *o*-nitrophenylhydrazone. This transformation, which is similar to that observed with the diazobenzene derivative of *o*-dinitrotoluene (compare preceding abstract), also takes place with substituted diazo-derivatives, the nitro-group entering the benzene nucleus in the ortho-position in cases where the para-position is occupied. The initial compounds formed from *o*-nitrophenylacetonitrile are, however, less stable than those yielded by *o*-dinitrotoluene, and undergo isomeric change so rapidly that they

cannot be obtained in the dry state. Still more unstable are the compounds formed by *o*-nitrotoluene with diazonium-salts, this reaction always giving *o*-nitrobenzaldehydephenylhydrazones. In the latter case, it is a hydrogen atom from the aliphatic carbon atom which converts the group $\cdot\text{N}:\text{N}\cdot$ into $:\text{N}\cdot\text{NH}\cdot$, whilst in the previous cases it is the hydrogen atom from the para- (or ortho-) position of the benzene nucleus.

Benzeneazo-o-nitrophenylacetonitrile, $\text{NO}_2\cdot\text{C}_6\text{H}_4(\text{CN})\cdot\text{N}:\text{NPh}$, forms a pale yellow, flocculent precipitate.

o-Cyanobenzaldehyde-*p*-nitrophenylhydrazone,
 $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)$,
 crystallises in yellow plates, m. p. $208-209^\circ$, dissolves in alkali hydroxides, forming intensely violet solutions, and, on reduction by means of tin and hydrochloric acid, yields benzoic and hydrocyanic acids and *p*-phenylenediamine.

o-Cyanobenzaldehyde-*o*-nitrophenylhydrazone, $\text{C}_{10}\text{H}_7\text{O}_2\text{N}_4$, crystallises in orange-red, flattened needles, m. p. 187° , gives a reddish-brown coloration when dissolved in alkali hydroxide solution, and yields benzoic and hydrocyanic acids and *o*-phenylenediamine when reduced with tin and hydrochloric acid.

o-Cyanobenzaldehyde-*p*-nitro-*o*-tolylhydrazone,
 $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NO}_2$,
 obtained by the isomeric change of *o*-tolueneazo-*o*-nitrophenylacetonitrile (prepared by the interaction of the sodium derivative of isonitrophenylacetonitrile and *o*-toluenediazonium acetate), crystallises from benzene in brownish-yellow needles, m. p. 188° , forms intensely violet solutions with alkali hydroxide, and yields benzoic and hydrocyanic acids and 2 : 5-tolylenediamine on reduction.

o-Cyanobenzaldehyde-*o*-nitro-*p*-tolylhydrazone,
 $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NO}_2$,
 formed by the isomeric transformation of *p*-tolueneazonitrophenylacetonitrile, crystallises in orange-red needles, m. p. 160° , gives a wine-red coloration with alkali hydroxides, and yields benzoic and hydrocyanic acids and 3 : 4-tolylenediamine on reduction.

o-Cyanobenzaldehyde-*o*-chloro-*p*-nitrophenylhydrazone,
 $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{NO}_2$,
 prepared from *o*-chlorobenzenediazonium acetate and the sodium derivative of *o*-isonitrophenylacetonitrile, forms orange-coloured needles, m. p. 182° , and gives violet-red solutions with alkali hydroxides.

o-Cyanobenzaldehyde-*p*-chloro-*o*-nitrophenylhydrazone, formed from *p*-chlorobenzenediazonitrophenylacetonitrile by isomeric change, crystallises in brownish-yellow laminae, m. p. 240° , and gives intensely violet solutions with alkali hydroxides in presence of a small quantity of alcohol.

o-Cyanobenzaldehyde-*o*-*p*-dinitrophenylhydrazone,
 $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$,
 formed by isomeric change of either *o*- or *p*-nitrobenzenediazonitrophenylacetonitrile, crystallises in reddish-brown prisms, m. p. 246° (decomp.), and gives intensely violet solutions with alkali hydroxide in presence of a drop of alcohol.

T. H. P.

Limiting Cases between Polymorphism and Isomerism. ROBERTO CIUSA and MAURICE PADOA (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 621—626).—*m*-Nitrobenzaldehydephenylmethylhydrazone forms two modifications, one red and the other yellow, both having m. p. 120—125° (Labhardt and Zembruski, Abstr., 1900, i, 125, found 112°, and Bamberger and Pemsel, Abstr., 1903, i, 286, 112—113°), at which temperature mixtures of the two also melt. The yellow form has the normal molecular weight in freezing benzene, the solution depositing the red modification on evaporation. Certain solvents, such as chloroform and benzene, convert the yellow into the red form, which may also be obtained by strongly cooling solutions of the yellow modification, or by seeding an alcoholic solution of either form with the red crystals. The red modification passes into the yellow on boiling with alcohol or ethyl acetate, on seeding its alcoholic solution with a yellow crystal, or on prolonged immersion in water or alcohol. There is no apparent or spectroscopic difference between solutions of the two products even when these are freshly dissolved. Both forms give with picryl chloride one and the same additive compound, which undergoes a considerable amount of dissociation even in concentrated alcoholic solution, giving the red hydrazone.

p-Nitrobenzaldehydephenylmethylhydrazone also occurs in two forms, one red and the other yellow, both having m. p. 130° (Labhardt and Zembruski, *loc. cit.*, found 132°). In this case, too, each form can be transformed into the other, but the change in colour is less distinct than with the meta-isomeride, and the red modification is very unstable unless stored under special conditions. *o*-Nitrobenzaldehydephenylmethylhydrazone occurs only in a red form, m. p. 90° (Labhardt and Zembruski, *loc. cit.*, found 77°), but *m*-nitroanisaldehyde-*p*-nitrophenylhydrazone, which is yellow when perfectly dry, becomes red immediately in moist air (Abstr., 1907, i, 137).

The criteria given by Wegscheider (Abstr., 1902, ii, 126) are insufficient to indicate whether this phenomenon is a case of isomerism or one of polymorphism. In this and in other cases, the phenomena of polymorphism and of isomerism approach so closely that the existence of a line of demarcation is not evident (compare Fock, this vol., ii, 23).

T. II. P.

Pantachromism of Dimethyl- and Diphenyl-violurates. ARTHUR HANTZSCH and ROBERT ROBISON (*Ber.*, 1910, 43, 45—68. Compare Abstr., 1909, i, 331, 333, 335).—In addition to the yellow lithium dimethylviolurate (*loc. cit.*, i, 335), a red salt, $C_6H_5O_2N_3Li$, has been prepared. It yields carmine-red compounds with $1EtOH$ and $1H_2O$. The yellow salt becomes red in the presence of traces of water. The solutions of the two lithium salts in pyridine are red, and in phenol, orange-coloured. A yellow compound with phenol, $C_6H_5O_2N_3Li \cdot PhOH$, is described; it loses phenol when exposed to the air, and forms the red hydrated salt.

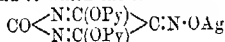
When the violet sodium salt is exposed to the air, it absorbs moisture (1 mol.) and becomes red. A red anhydrous sodium salt can be prepared by heating the compound containing ethyl alcohol. The

compound with phenol (1PhOH) is yellow, and when heated at 100° with methyl alcohol yields the anhydrous red salt. The blue potassium salt when exposed to the atmosphere yields the violet hydrate ($\frac{1}{2}\text{H}_2\text{O}$); the corresponding phenol compound has a rose-red colour.

The bluish-violet rubidium salt (*loc. cit.*, 334) contains $0.5\text{H}_2\text{O}$, and when boiled with methyl alcohol yields a pure blue anhydrous salt; the phenol compound has a rose-red colour. The caesium salt crystallises from alcohol in deep indigo-blue needles, and yields a rose-red phenoxide. Dimethylvioluric acid and phenol yield a yellow additive compound. Two coloured silver pyridine salts, $\text{C}_6\text{H}_5\text{O}_4\text{N}_3\text{Ag} \cdot \text{C}_5\text{NH}_5$, have been prepared: a labile green salt by the addition of ether to the pyridine solution of brown silver dimethylviolurate, and a stable bluish-violet salt obtained when the green salt is left in contact with ether and pyridine.

The methylamine salt, $\text{C}_6\text{H}_5\text{O}_4\text{N}_3 \cdot \text{NH}_2\text{Me}$, has a rose-red colour, and when exposed to the air yields the yellow acid salt; the dimethylamine salt is violet, the normal trimethylamine salt is blue, the acid salt orange-yellow, and the tetramethylammonium salt is blue. The ethylamine salts are very similar. The normal tripropylamine salt could not be isolated; the acid salt, $2\text{C}_6\text{H}_5\text{O}_4\text{N}_3 \cdot \text{NPr}_3$, is orange-yellow. The dibenzylamine salt exists in a labile red and a stable bluish-violet modification. Piperidine yields a stable blue and a labile red salt, $\text{C}_6\text{H}_5\text{O}_4\text{N}_3 \cdot \text{C}_5\text{H}_{11}\text{N}$. Pyridine yields a stable yellow acid salt.

Diphenylvioluric acid was prepared by a modification of Whiteley's method (*Trans.*, 1907, 91, 1330); the pure neutral salts are best prepared in alcoholic solution, as they readily decompose in the presence of aqueous alkalis. They crystallise with alcohol, which can be completely removed by heating the very finely divided salt. The lithium and sodium salts exist in labile red and stable yellow modifications, and yield red compounds with 1EtOH. The ammonium salt forms a violet compound with EtOH. The normal potassium, rubidium, and caesium salts are blue, and the acid rubidium and caesium salts green; the magnesium and zinc salts are yellow; the thallous silver salts exist in stable green and labile colourless forms. The acid silver salt, $\text{C}_{12}\text{H}_{10}\text{O}_8\text{N}_6\text{Ag} \cdot 3\text{H}_2\text{O}$, has an orange colour. The salts of dimethyl- and diphenyl-violuric acids exhibit both pantachromism and chromotropism. The labile forms of the salts are usually stable when perfectly dry, but pass readily into the more stable forms in the presence of a little water or alcohol. An increase in the depth of colour of the salts is observed as the metallic radicle becomes more positive, and in the case of substituted ammonium salts an increase in depth of colour is observed with an increase in the number of alkyl groups. The addition of phenol to the molecule of the alkali salts results in a diminution of colour, whereas the addition of pyridine produces an increase in colour, except in the case of the compound of silver violurate and pyridine, which is colourless, and to which the formula



is ascribed.

An increase in the depth of colour with an increase in the positive

nature of the metallic radicle is noticed in the case of concentrated aqueous or alcoholic solutions, and also of solutions in non-ionising solvents, such as chloroform or phenol. A negative solvent tends to lessen the depth of colour of the solution of any given salt. Molecular-weight determinations in phenol and ethyl acetate indicate that the different coloured isomeric salts are unimolecular.

The absorption spectra solutions of the acids and of their alkali salts have been measured.

A comparison of the absorption curves for diphenylvioluric acid, its lithium and cesium salts, and nitrosoisopropylacetone (Baly and Desch) points to the conclusion that the blue violurates should be represented as nitroso-enolic salts: $\text{CO} \begin{smallmatrix} \text{NR} \cdot \text{CO} \\ \text{NR} \cdot (\text{COMe}) \end{smallmatrix} \text{C} \cdot \text{NO}$.

The violuric acids as true oximino-ketones are the more completely transformed into the structurally isomeric nitroso-enols the more positive the nature of the metallic radicle present and the solvent.

J. J. S.

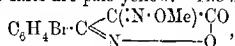
Pantachromic Salts of Oximino-oxazolones. ARTHUR HANTZSCH and J. HEILBRON (*Ber.*, 1910, 43, 68—82. Compare Hantzsch and Kemmerich, *Abstr.*, 1909, i, 336).—*p*-Bromo- and *p*-methoxy-derivatives of oximinophenylloxazolone yield pantachromic salts with colourless bases. The esters and acyl derivatives on the other hand are only pale yellow. The salts of the bromo-derivative are comparatively stable, and dissolve in various neutral solvents. Molecular-weight estimations in acetone, pyridine, and chloroform indicate that the salts, both ammonium and metallic, are unimolecular in solution. The colours of the salt solutions in non-ionising media increase in depth with the positive nature of the metallic radicle present.

The absorption spectra, both visible and ultra-violet, of the oxazolones and their salts in different solvents have been tabulated. The free acids are true oximino-compounds, and their absorption spectra resemble those of their ethers and acyl derivatives. The phenolic solution of the oximino-compound is distinctly yellow. The ultra-violet spectra of the salts do not differ materially from those of the free acids, but the visible spectra of the salts show characteristic absorption bands which are not present in the spectra of the free acids. The blue solutions of the potassium, rubidium, cesium, and tetra-alkylammonium salts give practically identical spectra. The conclusion is drawn that the yellow salts derived from feeble bases possess the true oximino-ketone structure, whereas the blue salts derived from strong bases have a nitroso-enolic structure.

p-Bromophenylloxazolone, prepared from ethyl *p*-bromobenzoylacetate and hydroxylamine, crystallises in glistening plates, m. p. 118° (decomp.), and reacts with nitrous acid, yielding oximino-*p*-bromophenylloxazolone, $\text{C}_6\text{H}_4\text{Br} \cdot \text{C} \begin{smallmatrix} \text{N} \\ \text{C}(\text{N} \cdot \text{OH}) \cdot \text{CO} \end{smallmatrix}$ which crystallises as a pale yellow monohydrate. The anhydrous compound has a pure

yellow colour and decomposes at 166° . The salts readily decompose in aqueous alkaline solutions, but are stable in alcoholic solution. The *lithium* salt, $C_6H_4O_3N_2BrLi$, exists in a stable yellow form only; the *sodium* salt forms orange-red needles, which form a pale rose-coloured *monohydrate*. The *potassium* salt exists in a rose-red and a reddish-violet form, and forms a pale red *phenol* compound, $C_6H_4O_3N_2BrK \cdot C_6H_5 \cdot OH$. The *acid potassium* salt is yellow. Rose, blue, and violet *rubidium* salts have been prepared; the *acid* salt is golden-yellow, and the *phenol* compound, pale red. Rose-coloured and bluish-violet *caesium* salts, together with pale red *phenol* compound, are described. The *barium* salt, $(C_6H_4O_3N_2Br)_2Ba \cdot 4H_2O$, is red, but when dehydrated is orange-coloured. Similar *calcium* and *magnesium* salts have been obtained. The *zinc* salt, $(C_6H_4O_3N_2Br)_2Zn$, is pale yellow, the *lead* salt pale rose, and the *thallium* salt flesh-coloured. A *blue*, an *orange*, and a *flesh-coloured silver* salt have been prepared, and a carmine-red monohydrate; the orange and the blue salts yield the same methyl ether. The silver salts are insoluble in neutral media, but dissolve in pyridine, yielding dichromatic solutions. The following additive compounds are described: $C_6H_4O_3N_2BrAg \cdot 2C_2H_5N$, violet; $C_6H_4O_3N_2BrAg \cdot 2NH_3$, deep blue; $C_6H_4O_3N_2BrAg \cdot NH_3$, rose; $C_6H_4O_3N_2BrAg \cdot CH_3CN$, carmine-red.

The *ammonium* salt is orange-coloured; the *methylamine*, *ethylamine*, *propylamine*, and *benzylamine* salts are rose-coloured; the *dimethylamine* and *diethylamine* salts are salmon-red; the *dipropylamine* salt, orange-coloured; the *dibenzylamine* salt, red; the *trimethylamine* salt, violet; the *triethylamine* salt, bluish-violet; the *tripropylamine* salt is red, and the *quaternary ammonium* salts crystallise in deep blue plates and their solutions resemble those of the alkali salts. The normal *pyridine* and *picoline* salts are pale yellow. The *methyl ether*,



forms pale yellow crystals, m. p. 129° (decomp.). The *acetyl* derivative also forms yellow crystals, m. p. 161° (decomp.), and the *benzoyl* derivative decomposes at 167° .

Anisylloxazolone, $OMe \cdot C_6H_4 \cdot C \begin{array}{l} \nearrow CH_2 \cdot CO \\ \searrow N \text{---} O \end{array}$, forms crystals with a satiny lustre, and m. p. $140-141^{\circ}$ (decomp.). The *oximino*-derivative, $OMe \cdot C_6H_4 \cdot C \begin{array}{l} \nearrow C(NOH) \cdot CO \\ \searrow N \text{---} O \end{array}$, forms a yellow *monohydrate*; the anhydrous compound has a deeper yellow colour, and decomposes at 149° . The salts are not so polychromatic as those of the corresponding bromine derivatives.

The following salts are described: *Sodium*, $C_{10}H_7O_4N_2Na$, orange-red; *potassium*, reddish-purple needles; *caesium*, bluish-violet; *ammonium*, red; *silver*, labile rose-coloured and stable blue; $C_{10}H_7O_4N_2Ag \cdot 2NH_3$, red. The *methyl ether*, $C_{11}H_{10}O_4N_2$, crystallises in pale yellow needles, m. p. 126° , and when hydrolysed yields *anisylfurazancarboxylic acid*, $OMe \cdot C_6H_4 \cdot C \begin{array}{l} \nearrow C(CO_2H) \cdot N \\ \searrow N \text{---} O \end{array}$, m. p. $99-100^{\circ}$. This acid is undoubtedly formed by the addition of water

and the opening of the oxazolone ring, and the subsequent elimination of methyl alcohol. J. J. S.

Pantachromism of Violurates and Salts of Analogous Oximino-ketones. ARTHUR HANTZSCH (*Ber.*, 1910, 43, 82—91).—The following general conclusions are given: (1) all polychromatic salts are unimolecular in solution, pointing to the isomerism and not polymerism of different coloured salts derived from the same metal; (2) the solutions pass from yellow or orange through red and violet to blue as the positive nature of the metallic radicle increases; (3) the absorption curves of yellow solutions are somewhat analogous to the curves for solutions of the free oximino-ketones in indifferent solvents and to solutions of their acyl and methyl derivatives. Deep blue solutions, on the other hand, show distinct selective absorption, and are optically closely related to blue aliphatic nitroso-compounds. The change in colour is attributed to a chemical change, namely, to the passage from the oximino-ketone form to the nitroso-enolic form: $O:C:C:N\cdot OH \rightarrow OH\cdot C:C:NO$.

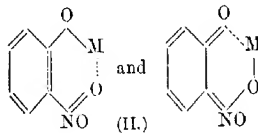
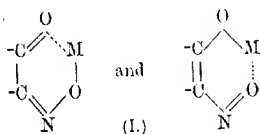
All solutions of the salts consist of an equilibrated mixture of the two forms, the proportions of each depending on the positive character of the metallic or substituted ammonium radicle present, and also on the nature of the solvent. It is shown that a mixture of the yellow

acetone solution of zinc diphenyl-violurate with the blue acetone solution of potassium diphenylviolurate is red and not green.

Leuco-salts yield yellow solutions, indicating a partial conversion into the nitroso-enolic form. The solid salts of orange, red, or purple colour are also regarded as mixed crystals of the two isomeric salts.

When a salt exists in a yellow and a blue form, these are regarded as isomeric in the sense of Werner's valency-isomerism (for example, I).

Similarly, the yellow and red salts

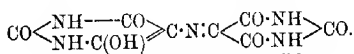


of nitrophenol are represented as (II)

The red *aci*-ethers are regarded as analogous to the red salts.

J. J. S.

Purpuric Acid. ARTHUR HANTZSCH and ROBERT ROBISON (*Ber.*, 1910, 43, 92—95).—The formula of Piloty and Slianner and Stieglitz (*Abstr.*, 1904, i, 634) for purpuric acid is analogous to that of the blue violurates: $CO \begin{smallmatrix} \text{NH} \text{---} \text{CO} \\ \text{NH} \cdot \text{C}(\text{OH}) \end{smallmatrix} \text{C} \cdot \text{NO}$ and



It has not been found possible to prepare coloured ethers or to isolate the pure-violuric acid. A method is recommended for the preparation of pure murexide (ammonium purpurate) (compare

Hartley, *Trans.*, 1905, **87**, 1981). The values for the electrical conductivity of the pure salt are: $\mu_{250} = 51.2$, $\mu_{512} = 51.5$, $\mu_{1024} = 51.8$, and $\mu_{\infty} = 52.9$. The conductivity of the system: murexide + HCl = purpuric acid + NH_4Cl has been determined at 0° . The purpuric acid is only slowly transformed into uranil and alloxan, and becomes colourless after three days. The initial value for μ_{512} is 225, but this gradually falls to 167 after twenty-five minutes, and to 21 after three days.

The value μ_{∞} for purpuric acid at 0° has been found to be 248.8 from the equation

$$\begin{array}{rcccl} \mu_{\infty} & \text{HCl} - \mu_{\infty} & \text{NH}_4\text{Cl} + \mu_{\infty} & \text{murexide} = \mu_{\infty} & \text{purpuric} \\ 278.8 & & 82.9 & 52.9 & 248.8 \end{array}$$

acid. The degree of dissociation at 0° and v_{512} is thus 0.9, and $K = 0.0158$.

Alloxan is not regarded as a quinonoid substance, since it shows only general absorption. J. J. S.

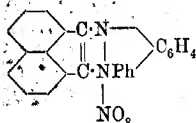
Synthesis of 5:7:5':7'-Tetrachloroindigotin. ERWIN OBERREIT (*Compt. rend.*, 1910, **150**, 282—283. Compare Danaïla, this vol., i, 137).—The constitution of this substance follows from the fact that it may be prepared from dichloroglycine-*o*-carboxylic acid which has been obtained from 3:5-dichloroanthranilic acid. W. O. W.

Quinoline-Red. EDUARD VONGERICHTEN and L. KRANTZ (*Ber.*, 1910, **43**, 128—130).—Quinoline-red is obtained by the interaction of molecular proportions of benzotrichloride, quinaldine, and isoquinoline in presence of zinc chloride (Hofmann, *Abstr.*, 1887, 380). When oxidised with potassium dichromate, a base is formed, m. p. 125° , which is regarded as *quinolyl isoquinolyl ketone*, $\text{C}_9\text{H}_6\text{N} \cdot \text{CO} \cdot \text{C}_9\text{H}_6\text{N}$, since on heating it with concentrated potassium hydroxide, isoquinoline and an acid, probably quinaldinic acid, are formed. The base dissolves with a yellow coloration in concentrated acids, and yields an intensely yellow-coloured, crystalline precipitate with phosphorus pentachloride in chloroform solution. The *oxime* forms somewhat grey-coloured, glistening plates, m. p. 245° . A second product of the oxidation is benzaldehyde. F. F. A.

Acenaphthene Series. FRITZ ULLMANN and ERWIN CASSIRER (*Ber.*, 1910, **43**, 439—445).—As acenaphthene is now a commercial product, the authors have attempted to convert it into dyes or into products from which dyes may be obtained.

A 40% yield of naphthalic acid can be obtained by oxidising acenaphthene with sodium dichromate and sulphuric acid (compare Graebe and Gfeller, *Abstr.*, 1892, 863). Naphthastyril (Ekstrand, *Abstr.*, 1886, 715; 1889, 52) is formed when naphthalimide is treated with sodium hydroxide solution and then with sodium hypochlorite at 15 — 25° . It reacts with 10% sodium hydroxide solution and *p*-toluenesulphonic chloride, yielding 8-*p*-toluenesulphonylamino-naphthoic acid, $\text{C}_6\text{H}_7\text{SO}_2 \cdot \text{NH} \cdot \text{C}_{10}\text{H}_6\text{CO}_2\text{H}$, as colourless needles, m. p. 158 — 159° (decomp.). With acetic anhydride the acid yields *p*-toluenesulphonylnaphthastyril, $\text{C}_{15}\text{H}_{13}\text{O}_2\text{NS}$, as straw-yellow, glistening needles, m. p. 174° .

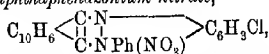
Phenylacenaphthaphenazonium nitrate (annexed formula), obtained from acenaphthenequinone, α -aminodiphenylamine, and acetic and nitric acids, crystallises in glistening, yellow needles. It dyes cotton mordanted with tannin a pale lemon-yellow. The *zincochloride*, $2C_{24}H_{15}N_2ZnCl_3$, forms yellow plates with a brassy lustre; the *dichromate*,



$(C_{21}H_{15}N_2)_2Cr_2O_7$, forms a yellowish-brown, crystalline powder, and the free base, $C_{25}H_{15}N_2\cdot OH$, a yellowish-

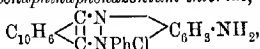
green precipitate. The *methyl ether*, $C_{25}H_{15}ON_2$, forms glistening, yellow crystals, m. p. $180-185^\circ$.

3-Chlorophenylacenaphthaphenazonium nitrate,

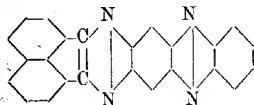


obtained from acenaphthenequinone and 5-chloro-2-aminodiphenylamine, forms yellow needles, and dyes cotton mordanted with tannin a yellowish-green. The *methyl ether*, $C_{25}H_{17}ON_2Cl$, forms pale green, glistening plates, and has m. p. $200-220^\circ$.

2-Aminophenyl-acenaphthaphenazonium chloride,



crystallises in deep violet-coloured needles, and dyes mordanted cotton Bordeaux-red. The *nitrate*, $C_{24}H_{16}O_3N_4$, crystallises in violet plates. The *acetyl derivative*,



$C_{26}H_{15}ON_3Cl$, crystallises in long, red needles.

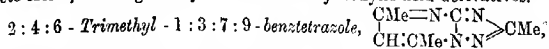
Acenaphthaphenazine (annexed formula), obtained by condensing acenaphthenequinone and 2:3-diaminophenazine in acetic acid solution, crystallises in red needles, which are not molten at 320° .

J. J. S.

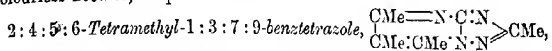
Methylene-Blue. PAUL LANDAUER and HUGO WEIL (*Ber.*, 1910, 43, 198-203).—Dürschnabel has shown (*Dis.*, Giessen, 1907) that indamines, oxazines, thiazines, and other para-quinonoid substances are converted by sulphurous acid or hydrogen sulphite into sulphonated leuco-compounds, whilst ortho-quinonoid substances, such as the indulines and safranines, are not reduced, and usually form sparingly soluble sulphites. The authors find that phenylhydrazine acts in a similar way. Methylene-blue, suspended in alcohol, is treated with phenylhydrazine at the ordinary temperature; after half an hour's warming on the water-bath, the system is allowed to cool in carbon dioxide or coal gas. Nitrogen is evolved, and leuco-methylene-blue, m. p. 185° , is obtained in yellow needles. The leuco-compound is stable in dry oxygen, and in the presence of alkaline oxidising agents can be directly acetylated by acetic anhydride, and yields a yellow *sodium* salt with alcoholic sodium ethoxide. Methylene-green by similar treatment yields brown needles of *nitroleucomethylene-blue*, $C_{16}H_{18}O_2N_4S$, m. p. $146-147^\circ$.

C. S.

Synthesis of Hetero-condensed, Heterocyclic Compounds with Two Nucléi: Derivatives of 2-Methyl-1:3-triazo-7:0 $\frac{1}{2}$ -pyrimidine [2-Methyl-1:3:7:9-benzotetrazole] from 5-Amino-2-methyl-1:3:4-triazole. CARL BULOW and KARL HAAS (*Ber.*, 1910, 43, 375—381. Compare Abstr., 1909, i, 614, 615 (and Errata), 1470; this vol., i, 80, 81).—5-Amino-2-methyl-1:3:4-triazole contains a labile hydrogen atom attached to the nitrogen next the basic group. Accordingly, it interacts with 1:3-diketones, forming di- and tri-alkyl or aryl derivatives of 2-methyl-1:3:7:9-benzotetrazole, or with keto-esters, forming methyl benzotetrazolehydroxylic acid derivatives.



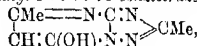
prepared by interaction of the aminotriazole with acetylacetone, forms colourless needles, m. p. 141—142°.



obtained in a similar manner from methylacetylacetone, has m. p. 116—117°.

4-Phenyl-2:6-dimethyl-1:3:7:9-benzotetrazole forms colourless, radially grouped, long, thin prisms, m. p. 110—111°.

4-Hydroxy-2:6-dimethyl-1:3:7:9-benzotetrazole,



obtained by boiling aminomethyltriazole with ethyl acetoacetate in glacial acetic acid solution, separates in glistening crystals, m. p. above, 280°. This and the following compounds are acidic, forming salts with alkalis. These react neutral in aqueous solution, and give amorphous or crystalline precipitates with salts of the heavy or alkaline-earth metals. Thus the lead salt forms short plates; the copper salt, bright green needles; the zinc salt, stellar aggregates of needles; the calcium salt, glistening needles.

4-Hydroxy-2:6-dimethyl-5-ethyl-1:3:7:9-benzotetrazole, prepared from ethyl ethylacetoacetate, has m. p. 262°, and forms soluble neutral salts, which are not decomposed by carbon dioxide.

4-Hydroxy-6-phenyl-2-methyl-1:3:7:9-benzotetrazole, obtained from ethyl benzoylacetate, forms long, colourless needles, which do not melt at 293°.

E. F. A.

Yellow and Red Forms of Salts and Hydrates of Hydroxy-azo-derivatives. ARTHUR HANTZSCH and PHILIP W. ROBERTSON (*Ber.*, 1910, 43, 106—122. Compare Tuck, *Trans.*, 1907, 91, 450; Gorke, Köppe, and Staiger, *Abstr.*, 1908, i, 477).—The salts of hydroxy-azo-compounds appear to exist in yellow and red modifications similar to the yellow and red salts of nitrophenols. It is only in the case of silver salts that yellow and red isomeric salts have been obtained from the same compound. Salts of the type $\text{R}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{OM} + 0.5\text{MeOH}$ (EtOH , $\text{CH}_3\cdot\text{CO}_2\text{Et}$, COMe , or $\text{C}_6\text{H}_5\text{N}$) are common; they are orange-coloured, and are regarded as compounds of 1 mol. of red salt, 1 mol. of yellow salt, and 1 mol. of the crystallising medium. When the last is removed, they yield red or yellow salts, or, sometimes, orange-coloured salts.

The following table gives the colours of the salts of four hydroxyazo-compounds:

	Benzene- azophenol.	p-Chlorobenzene- azophenol.	p-Bromobenzene- azophenol.	Benzene- azo-o-di- bromophenol.
H.....	Yellow	Yellow	Yellow	Orange
Li	Pale yellow	Pale yellow	Pale yellow	Pale yellow
Na	Orange	Orange	Orange	Yellow
K.....	Red	Pale red	Red	Orange
Rb	Dark red	Orange	Red	Orange
Cs	Pale red	Red	Red	Orange
Ag	(Yellow (stable) Red (labile))	Yellow (stable) Red (labile)	Yellow (stable) Red (labile)	Red

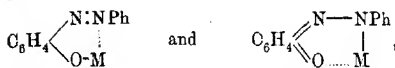
It is noticeable that the lithium salts are paler in colour than the original hydroxy-derivatives, and that, as a rule, the caesium salts are paler than the rubidium.

The hydrates of hydroxyazo-compounds also appear as representatives of two chromo-isomeric series.

The following are the colours of the hydroxyazo-compounds and of their hydrates (0.5 or 1 mol. H_2O): o-Chlorobenzeneazophenol, red, yellow; meta-compound, yellow, red; para-compound, yellow, yellowish-red; o-bromobenzeneazophenol, red, yellow; meta-compound, yellow, red; para-compound, yellow, red; o-tolueneazophenol, yellow, yellow; meta-compound, yellow, yellow; benzeneazo-m-cresol, yellow, yellow; m-chlorobenzeneazo-m-cresol, yellow, red; o-tolueneazo-m-cresol, yellowish-red, yellowish-red; benzeneazo-o-chlorophenol, yellowish-red (labile), yellow (stable), yellowish-red. The last-mentioned colour in each case refers to that of the hydrate.

The determinations of the absorption spectra and of the molecular extinctions of solutions of the salts and hydrates show that the yellow and red forms are not polymorphous or polymeric. The solutions in indifferent solvents have much the same colours as the solid salts. The nature of the solvent also affects the colour of the solutions, the more positive the nature of the solvent (namely, pyridine) the deeper the colours. These solutions of salts of hydroxyazo-compounds are regarded as equilibrium mixtures of yellow and red salts, just as in the case of the violurates. From such solutions the orange-coloured additive compounds (1 mol. yellow, 1 mol. red, 1 mol. solvent) separate, as they are sparingly soluble. All these solid additive compounds have practically the same colour, so that the effect of different solvents on the solids is practically nil; since, however, the solutions have different colours it is probable that the relative amounts of red and yellow salts in the different solutions vary considerably. The increase in colour of the salts, as compared with the free hydroxy-compounds, indicates that salt formation as a rule favours the formation of the red form. It is shown that mere salt formation (Gerke) has not necessarily an auxochromic effect, since lithium salts are paler than the free hydroxy-compounds, and dipropylamine salts in some cases give absorption curves exactly analogous to those of the free hydroxy-compounds.

The following structural valency formulæ are suggested for the yellow and red forms:



where the dotted lines represent subsidiary valencies.

The following values for the molecular extinctions ($\lambda=546$) of hydroxyazobenzene and its salts in different media at 15° and $V=200$ are given :

Rubidium salt in pyridine 510, in ethyl acetate 81, in alcohol 44 ; caesium salt in alcohol 24, in benzene + 4% alcohol 18, in hexane + 4% alcohol 14 ; lithium salt in ether 12 ; dipropylamine salt + 100 mols. dipropylamine in benzene 9 ; hydroxyazobenzene in carbon tetrachloride 8, in chloroform 7, in pyridine 7, in benzene 7, in alcohol 4. The values for the molecular extinctions ($\lambda=546$) for salts of dibromohydroxyazobenzene at 15° and $V=400$ are :

Solvent.	Li.	Na.	K.	Rb.	Cs.
Ether	15	17	18	18	—
Alcohol	39	37	35	35	36
Pyridine.....	140	179	180	210	220

J. J. S.

Formation and Decomposition of Symmetrical Bisazo-compounds of Ethyl Arylhydrazonemesoxalylbishydrazonemalonylacetates and of Ethyl Malonylbishydrazonemalonylacetates. CARL BÜLOW and C. BOZENHARDT (*Ber.*, 1910, 43, 234—242).—Ethyl malonylbishydrazonemalonylacetate reacts with one molecule of benzenediazonium chloride, yielding ethyl phenylhydrazonemesoxalylbishydrazonemalonylacetate with 72% yield (compare Abstr., 1908, i, 253). In addition, small quantities of ethyl benzeneazoacetate, *cyclomalonylhydrazide*, and 4-benzeneazo-3-methyl-5-pyrazolone are formed. Ethyl phenylhydrazonemesoxalylbishydrazonemalonylacetate, when warmed with phenylhydrazine, decomposes into 4-benzeneazo-1-phenyl-3-methylpyrazolone (orange needles, m. p. $154-155^\circ$; yield 85%), 4-benzeneazopyrazolidone (m. p. 266°), and hydrazine. When boiled with dilute potassium hydroxide, it yields 4-benzeneazo-3-methyl-5-pyrazolone and mesoxalic acid-phenylhydrazone; whilst by the action of boiling acetic acid 4-benzeneazo-3-methyl-5-pyrazolone, ethyl benzeneazoacetate, and 4-benzeneazo-3:5-pyrazolidone are produced. Dimethyl mesoxalato-phenylhydrazone (compare Abstr., 1905, i, 90), when treated with hydrazine hydrate, yields *mesoxalylphenylhydrazonedihydrazide*, m. p. 164° . The *diacetyl* derivative has m. p. $246-247^\circ$. The dihydrazide condenses with ethyl benzeneazoacetate, giving ethyl phenylhydrazonemesoxalylbishydrazonemalonylacetate, the constitution of which is confirmed by this mode of preparation. The above dihydrazide when boiled with acetic acid also yields 4-benzeneazo-3:5-pyrazolidone of m. p. 266° , already mentioned. Ethyl phenylhydrazonemesoxalylbishydrazonemalonylacetate is also produced by condensing equimolecular quantities of benzenediazonium chloride and *ethyl malonylbishydrazonemalonylacetate*. The latter is

formed in 80% yield by the condensation of 2 molecules of ethyl benzeneazoacetate with malonyldihydrazide. It is decomposed by boiling alcohol into ethyl malonate and 4-benzeneazo-3-methyl-5-pyrazolone. On heating, it melts at 128°, then gas is evolved, and the mass solidifies, melting again at 217—218°. In this process the theoretical quantity of alcohol is evolved, and the residue consists of 4-benzeneazo-3-methyl-5-pyrazolone and 1:1-malonylbis-4-benzeneazo-3-methyl-5-pyrazolone (compare Abstr., 1907, i, 986), m. p. 225.5°. On boiling with potassium hydroxide or pyridine, the latter yields 4-benzeneazo-3-methyl-5-pyrazolone and malonic acid.

Ethyl malonylbishydrazoneacetate yields with 3 molecules of *p*-diazotoluene chloride, ethyl-*p*-tolylhydrazones-mesozalylbishydrazone-toluene-*p*-azoacetate, orange needles, m. p. 209—210°. By the condensation of malonyldihydrazide with ethyl toluene-*p*-azoacetate, ethyl malonylbishydrazonetoluene-*p*-azoacetate, orange needles, m. p. 114—115°, is produced.

R. V. S.

Azo-dyes derived from 2:4-Dimethylpyrrole and Hæmopyrrole. LEON MARCHLEWSKI and J. ROBEL (*Ber.*, 1910, 43, 260—266 *).—For the purpose of comparison with the azo-dyes obtained from hæmopyrrole and chlorophyllpyrrole, the authors have investigated the diazotisation of dimethylpyrrole. In addition to the monoazo-derivative of Plancher and Soncini (Abstr., 1901, i, 432), they have obtained small quantities of a substance, $C_{10}H_{12}N_6Cl$, which they suppose to have the formula: $(N_2Ph \cdot C_6H_7N \cdot C_6H_7N \cdot N_2Ph)HCl$. It crystallises in well-developed red needles having a metallic lustre, and it is only slightly soluble in most solvents. In physical characteristics (including the absorption spectrum) the substance shows similarity to the azo-derivative of hæmopyrrole.

R. V. S.

Reduction of Nitroso-derivatives of Acetyl- and Benzoylhydrazobenzene. LOUIS NOMBLOT (*Compt. rend.*, 1910, 150, 338—339).—*Nitrosoacetylhydrazobenzene*, $NAcPh \cdot NPh \cdot NO$, obtained by adding ethyl nitrite to acetylhydrazobenzene suspended in alcohol, occurs in yellow prisms, m. p. 65°. The corresponding benzoyl derivative crystallises in pale yellow leaflets, m. p. 116.5°. The action of reducing agents on these two substances has been studied. An alcoholic solution of hydrazine hydrate converts them into the corresponding acetylhydrazobenzene, with liberation of ammonia. Aluminium amalgam gives aniline, together with acetanilide or benzanilide. Zinc dust in presence of acetic acid at 0—5° gives no reduction products. Under no conditions were triazan derivatives obtained.

W. O. W.

[Preparation of *p*-Aminophenyl-2-azimino-5-naphthol-7-sulphonic Acid.] GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 214658).—*p*-Aminophenyl-2-azimino-5-naphthol-7-sulphonic acid, a grey, crystalline powder sparingly soluble in water and employed in the production of Bordeaux-red dyes, is prepared by the following series of operations:

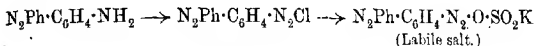
1-Chloro-2:4-dinitrobenzene is condensed with β -naphthylamine-

* and *Bull. Acad. Sci. Cracov*, 1910, A, 1—8.

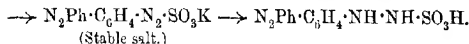
5:7-disulphonic acid, yielding 2:4-dinitrophenyl- β -naphthylamine-5:7-disulphonic acid; this is reduced with sodium sulphide and ammonium chloride to *p*-nitro-*o*-aminophenyl- β -naphthylamine-5:7-disulphonic acid, the disodium salt of which forms red, crystalline leaflets. This substance is treated with sodium nitrite in the presence of sulphuric acid, and the resulting nitroazimino-compound reduced with iron filings to *p*-aminophenyl-2-aziminonaphthalene-5:7-disulphonic acid, grey needles, which, on heating with sodium hydroxide solution at 180–190°, yields the foregoing naphtholsulphonic acid.

F. M. G. M.

Azoarylhydrazinesulphonic Acids. JULIUS TRÖGER and A. WESTERKAMP (*Arch. Pharm.*, 1909, 247, 657–698).—The hydrazinesulphonic acid, obtained by the action of sulphur dioxide on aqueous benzenediazonium sulphate (Abstr., 1904, i, 118; 1906, i, 120, 993, 994), has been synthesised by Tröger and Puttkammer (Abstr., 1907, i, 263) by converting diazotised aminoazobenzene into azobenzenediazosulphonate, and reducing the latter by ammonium sulphide:

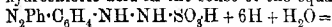


(Labile salt.)



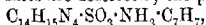
(Stable salt.)

This synthetic process has now been applied to numerous aminoazo-compounds, whereby hydrazinesulphonic acids are obtained, which are red, blue, violet, or brown; they are best purified by means of their salts with aromatic amines, and are reduced by stannous chloride and hydrochloric acid in the sense of the equation:

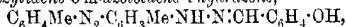


$\text{NH}_2\text{Ph} + \text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2 + \text{NH}_3 + \text{H}_2\text{SO}_4$,
a monoamine and a diamine always being formed. When heated with alcoholic hydrogen chloride and an aldehyde or ketone, the hydrazinesulphonic acids lose the sulphonic acid group, and are converted into hydrazones which form coloured salts with the hydrochloric acid.

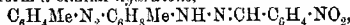
4-Amino-*o*-m-azotoluene thus yields a reddish-brown *o*-m-azotoluene-4-hydrazinesulphonic acid, $\text{C}_6\text{H}_4\cdot\text{Me}\cdot\text{N}_2\cdot\text{C}_6\text{H}_3\cdot\text{Me}\cdot\text{NH}\cdot\text{NH}\cdot\text{SO}_3\text{H}$ (the potassium and barium salts are described; the *p*-toluidine salt,



m. p. 158°, forms yellow needles), which yields *o*-toluidine and 1:2:5-tolylenediamine by reductive fission, and in the presence of alcoholic hydrogen chloride reacts with salicylaldehyde to form *o*-hydroxybenzylidene-*o*-m-azotoluene-4-hydrazone,



m. p. 130–131° (the hydrochloride, $\text{C}_{21}\text{H}_{21}\text{ON}_4\text{Cl}$, forms violet needles, and the sulphate, blue needles with a green reflex), with *p*-nitrobenzaldehyde to form a similar hydrazone.

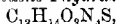


m. p. 158°, with *p*-methoxybenzaldehyde to form the reddish-yellow

hydrazone, $C_{22}H_{22}ON_4$, m. p. 147° , and with benzaldehyde to form an orange-red hydrazone, $C_{21}H_{20}N_4$, m. p. 160° .

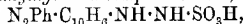
4-Amino-*mp*-azotoluene yields reddish-brown, amorphous *mp*-*azo*-toluene-4-hydrazinesulphonic acid, $C_{14}H_{14}O_3N_4S$, the *p*-toluidine salt of which, m. p. 183° , forms yellow needles; the hydrazone, $C_{22}H_{22}ON_4$, m. p. 148° , from *p*-methoxybenzaldehyde forms golden-yellow leaflets; the hydrazone, $C_{21}H_{20}ON_4$, m. p. $120-121^\circ$, from salicylaldehyde forms red prisms, and the hydrazone, $C_{21}H_{19}O_2N_4$, m. p. $176-177^\circ$, from *m*-nitrobenzaldehyde is a reddish-brown, crystalline powder.

op-Azotoluene-4-hydrazinesulphonic acid, $C_{14}H_{16}O_3N_4S$, obtained from 4-amino-*op*-azotoluene, is a dark reddish-brown, amorphous powder; the *p*-toluidine salt, m. p. 171° , forms reddish-yellow needles. *mp*-Azotoluene-6-hydrazinesulphonic acid, $C_{14}H_{16}O_3N_4S$, is an indigo-blue, amorphous powder obtained from 6-amino-*op*-azotoluene; the *p*-toluidine salt has m. p. 154° , and the aniline salt has m. p. 139° . Benzeneazo-*p*-toluene-4-hydrazinesulphonic acid,

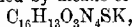


is a dark red, amorphous powder, which forms a yellow, crystalline *p*-toluidine salt, m. p. 170° (decomp.), and a *p*-xylydine salt, m. p. 175° (decomp.). Benzeneazo-*p*-xylydine, $N_2Ph \cdot C_6H_4Me_2 \cdot NH_2$, m. p. $104-105^\circ$, obtained by the slow addition of diazotised aniline hydrochloride to an alcoholic solution of *p*-xylydine and treatment of the resulting hydrochloride with ammonium hydroxide, separates from dilute alcohol in golden leaflets, and from petroleum and benzene as a deep orange, crystalline powder, and forms a nitrate crystallising in long, blue needles, a violet hydrogen sulphate, and a golden-yellow oxalate. It is converted by the usual processes into benzeneazo-2:5-xylylene-4-hydrazinesulphonic acid, $C_{14}H_{16}O_3N_4S$, a dark red, micro-crystalline powder, the reddish-yellow *p*-toluidine salt of which has m. p. 158° .

Benzeneazo- α -naphthylhydrazinesulphonic acid,



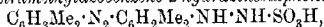
obtained from benzeneazo- α -naphthylamine, is an amorphous, violet powder, which is best purified by means of its potassium salt,



which crystallises in reddish-yellow needles. The acid is reduced by zinc dust and hot acetic acid, yielding aniline and 1:4-naphthylene-diamine, and reacts with alcoholic hydrogen chloride and aldehydes in the manner mentioned, hydrazones being produced in the form of hydrochlorides; the hydrazone, $N_2Ph \cdot C_{10}H_7 \cdot NH \cdot N \cdot CH \cdot C_6H_4 \cdot OMe$, m. p. $158-160^\circ$, from *p*-methoxybenzaldehyde forms orange needles (hydrochloride, deep blue needles); the hydrazone from salicylaldehyde has m. p. 205° (hydrochloride, bluish-violet needles); the hydrazone from *p*-nitrobenzaldehyde has m. p. $172-173^\circ$ (hydrochloride, dark green powder).

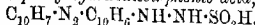
In a similar manner, benzeneazo- β -naphthylamine yields benzeneazo- β -naphthylhydrazinesulphonic acid, a coffee-coloured, amorphous powder, which is purified through the *p*-toluidine salt, m. p. 165° (decomp.).

2:4:3':5'-Tetramethylazobenzene-2-hydrazinesulphonic acid,



obtained from aminoazo-*m*-xylene, is a red, amorphous powder, which forms a *p*-toluidine salt, m. p. 170° (decomp.), aniline salt, m. p. 153° (decomp.), and a *p*-xylydine salt, m. p. 176° (decomp.).

α-Naphthylazo-*α*-naphthylhydrazinesulphonic acid,



obtained from aminoazo-*α*-naphthalene, is a dark blue substance.

C. S.

The Adsorption of Proteins. WILHELM BILTZ and HANS STAVER (*Biochem. Zeitsch.*, 1909, 23, 27—42).—The adsorption of egg-white by cellulose, iron hydroxide, and kaolin was estimated in varying concentrations of the protein. The amount adsorbed was determined by estimating the nitrogen in the clear solution, after filtration of the adsorbent, by a modification of Kjeldahl's method, the amount of ammonia being determined colorimetrically with the use of Nessler's reagent. The adsorption process is not entirely reversible, and the results do not entirely agree with the ordinary adsorption equation. The application of the adsorption formula to the combination of toxin and antitoxin was also investigated ($1 - T/n = \log k + 1/p \log T$, where T is the concentration of the free toxin, and $1 - T$ that of the combined). The results of the neutralisation of tetanolysin and streptolysin by the antilynsins, and of the streptolysin by cholesterol, of diphtherotoxin by its antitoxin, of saponin by ox-blood, of cobra-lysin by antivenin, and other similar reactions were investigated. The results obtained were compared with those calculated from the adsorption equation and Arrhenius' mass reaction equation. Neither of these equations agreed in a satisfactory manner with the results obtained experimentally.

S. B. S.

Composition of the Products of the Alkaline Hydrolysis of Crystalline Egg-albumin. NOGENDRAMOHON GUPTA (*Monatsh.*, 1909, 30, 767—771).—The products resulting from the hydrolysis of egg-albumin by sodium hydroxide (compare Skraup and Hummelburger, *Abstr.*, 1909, i, 340) have been submitted to careful analysis, with the following results:

	Carbon.	Hydrogen.	Nitrogen.	Sulphur.
Protalbic acid	55.4	7.2	14.3	2.4
Lysalbic „	52.9	7.0	14.9	1.2
Lysalbiupeptone	46.2	6.6	10.3	1.2

W. H. G.

The Preparation and Properties of Iodo-Mucoids. GUSTAVE M. MEYER (*J. Biol. Chem.*, 1909, 7, 11—16).—Iodo-mucoids were prepared by the action of iodine on tendo-mucoid in a dilute solution of sodium carbonate; they contain approximately 14% of iodine.

W. D. H.

The Relation of Proteins to Crystalloids. I. The Osmotic Pressure of Hæmoglobin and the Laking of Red Blood-corpuscles. HERBERT E. ROAF (*Quart. J. exp. Physiol.*, 1910, 3, 75—96).—A simple method is described for the direct measurement of the osmotic pressure of a solution when the solute does not pass

through parchment paper or other suitable membranes. In this way the osmotic pressure of laked corpuscles and crystallised hæmoglobin was measured, and pressures corresponding with the molecular weight of hæmoglobin calculated from other data were obtained if conditions obtain which limit ionisation; but otherwise much higher pressures are reached, and it is suggested that this is due to the ionising of hæmoglobin salts; both acid and alkali increase the pressure, and as with serum proteins, a minimal pressure is found near the neutral point. Many substances lower the osmotic pressure, and thus might help to prevent laking of red corpuscles. Pressures were obtained with corpuscles laked by freezing and thawing up to 282 and 256. If ionisation occurred, the calculated pressure might be as high as 960 mm. of mercury. With such a range of pressure, the osmotic pressure of hæmoglobin should be considered in discussing the laking of corpuscles, but until further experiment has determined the pressures in mixed solutions containing the various crystalloids of the corpuscle, it cannot be decided what part is played by hæmoglobin and how much is due to other factors. W. D. H.

Blood Colouring Matter. WILLIAM KÜSTER (*Ber.*, 1910, 43, 370—375).—The compound, $C_{30}H_{36}O_8N_4$, obtained by Küster and Fuchs (*Abstr.*, 1907, i, 572) as a bye-product of the action of aniline on hæmin is also formed in small quantity when acetyl hæmin is converted into dehydrochloride hæmin. By the action of concentrated hydrochloric acid under pressure on hæmatin, the organic material partly loses its acid properties and partly undergoes oxidation. Hæmin and hæmatin are regarded as ferric compounds, and the ferric chloride formed oxidises part of the iron-free hæmatin. The oxidation product does not undergo rearrangement to hæmatoporphyrin. When hydrogen bromide is used, the oxidising action of the ferric bromide is neutralised, and hæmatoporphyrin formation takes place. Ten % hydrochloric acid only eliminates 5% of the iron from hæmin at 130°, whereas under similar conditions over 90% of the iron is separated from hæmatin.

Hæmatin is slowly changed by solution in alkali, whereas the fresh solution is completely precipitated by the theoretical quantity of barium chloride. After keeping, a large excess of this is required. Polymerisation to a β -hæmatin takes place on keeping.

The conversion of hæmatin by reducing agents into hæmochromogen is regarded as corresponding with a reduction from the ferric to the ferrous state. Hæmoglobin contains ferrous iron; oxyhæmoglobin, however, contains iron peroxide.

Hæmin forms salts with 3 mols. of alkali hydroxide; dehydrochloride hæmin, salts with 2 mols. These can be dialysed in 1% solution without the dye passing through. Hæmin only takes up 2 mols. of sodium carbonate, and sodium hydrogen carbonate appears in the outer water on dialysis. Precipitates obtained with other metallic salts showed a very varying metal content.

The iron salts dissolve in sodium hydroxide and are acids; seemingly, the second iron atom is attached to the free nitrogen atom.

E. F. A.

Behaviour of Gelatinous Substances or Collagens towards Carbon Disulphide. WL. S. SADIKOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1597—1686; *Kolloid. Chem. Beihfte*, 1910, 1, 118—220).—When an alkali acts on glutin in presence of carbon disulphide, "thiohydration" occurs, this consisting of two distinct processes, namely, hydration by the alkali and subsequent addition of carbon disulphide or "thionylation" (compare Abstr., 1907, i, 740). The most characteristic part of the thionylglutin thus obtained is the complex to which the carbon disulphide is added, and which is termed the "receptor." This receptor is extremely indifferent, neither being destroyed by water, reacting with tannin, bromine, aldehydes, or the majority of organic acids, nor being replaced by benzoyl chloride or methyl iodide. It takes up carbon disulphide in neutral, alkaline, or acid media, combines with strong mineral acids, and with acetic and oxalic acids, is substituted by trinitrophenol and "immobilised," or rendered incapable of taking up carbon disulphide, by solutions of sulphates, probably owing to the sulphuric acid formed by adsorptive decomposition of the salts.

In the case of tendo-collagen, the receptor is not homogeneous. The predominating part of it is readily reactive, being replaced by carbonic acid, and by organic and mineral acids, acetic anhydride, benzoyl chloride, bromine, methyl iodide, or aldehydes; it is stable towards the action of heat or water, and is not replaced by picric acid. The lesser part of the receptor is highly inert, is replaceable only by mineral acids and tannin, and is stable towards the action of water, but thermo-labile; this part is not altered by the action of alkali hydroxide. The reactive portion of this receptor would seem to be a primary or secondary amine. T. H. F.

The Scission Products Resulting from the Partial Hydrolysis of Proteins. EMIL ANDERHALDEN (*Zeitsch. physiol. Chem.*, 1909, 63, 401—404).—From the partial hydrolysis of silk, glycyl-L-tyrosine was obtained previously. The present research gives details of the preparation and identification of another dipeptide from the same source, namely, *D*-alanyl-glycine. W. D. H. ‡

Trypsin and Antitrypsin. KURT MEYER (*Biochem. Zeitsch.* 1909, 23, 68—92).—Samples of dried pancreatic juice and juice from the small intestine were used in the experiment, and dissolved to give the necessary concentrations as required. The tryptic action was estimated by the Gross-Fuld caseinogen method. The influence of the quantity of kinase on the activation of the trypsinogen was first investigated. The results indicate that the kinase action is of ferment like character. The grade of activation is not proportional to the amount of kinase, and very small quantities of the latter can activate large quantities of the trypsinogen, provided that sufficient time is allowed for the action. The rate of activation is approximately proportional to the amount of kinase. The greater activity of mixtures containing large amounts of kinase is apparently due to: shortening of the activating process, owing to which the concurrent destruction of the trypsin and kinase becomes less marked. An excess of kinase does not inhibit the activation. The inhibitor

substance of the serum is neither an antikinase nor an antitrypsinogen. The former possibility is excluded by the fact that the anti-action is not overcome by the addition of excess of kinase, and is also exerted on trypsin which has been obtained from trypsinogen by calcium salts. Antitrypsinogen and antikinase are also excluded by the fact that the inhibitory action of the serum is not increased by allowing it to act on the kinase or trypsinogen alone before mixture, and that the quantity necessary for inhibiting a mixture which is being gradually activated depends on the amount of trypsin actually present at the time of addition.

No antitrypsinogen or antikinase could be obtained by immunisation experiments. The saturation of trypsin by the anti-substance follows the law of multiple proportions. In the fractional saturation of trypsin by the anti-substance, the Danyez phenomenon was observed, namely, the inhibitory action is weaker than if the whole quantity of anti-substance had been added at one time.

Previous treatment of trypsin by antitrypsin did not increase the inhibitory effect. The formation of a non-digesting, but anti-substance binding trypsinoid could not be effected. The effect of heating trypsin and the anti-substance was also investigated. The results indicate that antitrypsin is not a negative catalyst, but actually enters into combination with trypsin. No kind of specificity was noted in the case of antitrypsin. S. B. S.

Influence of the Reaction of the Medium on the Filtration of Diastases. MAURICE HOLDERER (*Compt. rend.*, 1909, 149, 1153—1156).—Details of experiments on extracts of *Aspergillus niger* are given, from which it appears that a porcelain filter is permeable to sucrase when the solution in which this is present is neutral to phenolphthalein; when the solution is neutral to methyl-orange, however, the ferment no longer passes the filter. In order, therefore, to render the extraction of sucrase more complete, it is desirable to have the solution alkaline whilst maceration is in process.

W. O. W.

Influence of the Reaction of the Medium on the Filtration of Malt Enzymes. MAURICE HOLDERER (*Compt. rend.*, 1910, 150, 285—288. Compare preceding abstract).—The enzymes of malt, amylase, dextrinase, and peroxydiastase resemble the diastases already studied in their behaviour when the solutions are filtered through porcelain. Filtration occurs readily when the solutions are neutral to phenolphthalein, but the passage of the enzymes through the filter is inhibited if the medium is neutral to methyl-orange. W. O. W.

Cellase and the Diastatic Decomposition of Cellose. GABRIEL BERTRAND and MAURICE HOLDERER (*Compt. rend.*, 1909, 149, 1385—1387).—An attempt to ascertain whether a specific ferment exists capable of hydrolysing cellose. Maltase and sucrase are without action on this substance, whilst a maceration of *Aspergillus niger* converts it completely into dextrose. Preparations of emulsin from almonds, and of emulsin with trehalase from barley or malt, have the same action. W. O. W.

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

	PAGE
XI.—3:5-Dichloro- <i>o</i> -phthalic Acid. By ARTHUR WILLIAM CROSSLEY and GERTRUDE HOLLAND WREN	98
XII.—The Constituents of <i>Colocyth</i> . By FREDERICK BELDING POWER and CHARLES WATSON MOORE	99
XIII.—A Contribution to the Study of the Oxydases. By ROSS AIKEN GORTNER, Ph.D.	110
XIV.—Experiments on the Walden Inversion. Part III. Optically Active β -Hydroxy- β -phenylpropionic Acids and the Corresponding β -Bromo- β -phenylpropionic Acids. By ALEX. MCKENZIE and HERBERT BROOKE PERREN HUMPHRIES	121
XV.—The Triazo-group. Part XI. Substituted Triazomalonic and Phenyltriazooacetic Acids. By MARTIN ONSLOW FORSTER and ROBERT MÜLLER	126
XVI.—Organic Derivatives of Silicon. Part XII. Dibenzyl-ethylpropylsilicane and Sulphonic Acids Derived from it. By FREDERICK CHALLENGER, B.Sc., and FREDÉRIC STANLEY KIPPING	142
XVII.—The Influence of Various Substituents on the Optical Activity of Tartramide. Part III. Halogen-substituted Anilides. By PERCY FARADAY FRANKLAND and DOUGLAS FRANK TWISS	154
THOMSEN MEMORIAL LECTURE. By SIR EDWARD THORPE, C.B., LL.D., F.R.S.	161
XVIII.—Formation of Heterocyclic Compounds. Part II. Action of Bases on the <i>aa'</i> -Dibromo-derivatives of Certain Dicarboxylic Acids. By HENRY RONDEL LE SUEUR and PAUL HAAS	173
XIX.—The Half-life Period of Radium; a Correction. By ROBERT WHITLAW GRAY and SIR WILLIAM RAMSAY, K.C.B.	185

XX.—The Intramolecular Rearrangement of Diphenylamine ortho-Sulphoxides. Part II. By EDWARD DE BARRY BARNETT and SAMUEL SMILES	186
XXI.—The Adsorption of Uranium-X by Barium Sulphate. By ARTHUR JOHN BERRY, B.A.	196
XXII.—2-Phenyl-1:3-benzoxazine-4-one. By ARTHUR WALSH TITHERLEY	200
XXIII.—Iodobenzenemonosulphonic Acid. Part II. Esters and Salts of Di- and Tri-iodobenzenesulphonic Acids. By MARY BOYLE	211
XXIV.—A Natural Substantive Dyestuff. By ARTHUR GEORGE PERKIN	220
XXV.—The Effect of Contiguous Unsaturated Groups on Optical Activity. Part IV. Conjugated Systems containing more than Two Unsaturated Groups. By SYDNEY ROBERT EDMINSON and THOMAS PERCY HILDITCH	223
XXVI.—The Constituents of Red Clover Flowers. By FREDERICK BELDING POWER and ARTHUR HENRY SALWAY	231
XXVII.—The Triazo-group. Part XII. Derivatives of <i>para</i> -Triazobenzaldehyde. By MARTIN ONSLOW FORSTER and HILDA MARY JUDD	254
XXVIII.— <i>iso</i> Quinoline Derivatives. Part IV. ortho-Dihydroxy-bases. The Conversion of 1-Keto-6:7-dimethoxy-2-alkyltetrahydro <i>iso</i> quinolines into 3:4-Dihydroxyphenylethylalkylamines. By FRANK LEE PYMAN	264
XXIX.—The Absorption Spectra of Naphthalene and of Tetramethylnaphthalene. By ANNIE HOMER and JOHN EDWARD PURVIS	280
XXX.—The Alkaloids of Ergot. Part II. By GEORGE BARGER and ARTHUR JAMES EWINS	284
XXXI.—The Action of Chlorine on Phenylcarbamide. By FREDERICK DANIEL CHAITAWAY and NEWCOMB KINNEY CHANEY	293
XXXII.— Δ^1 -Nonylenic Acid. By VICTOR JOHN HARDING and CHARLES WEIZMANN	299
XXXIII.—Strychnine, Berberine, and Allied Alkaloids. By WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON	305

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS :-

PART I.

Organic Chemistry.

	PAGE
MANCHOT (WILHELM) and W. BRANDT. Cuprous Compounds of Ethylene and of Carbon Monoxide	i, 85
DOROSCHESKY (ANTONY G.) and M. S. ROSCHDESTVENSKY. Specific Gravity of Solutions of Alcohols: Mixtures of Propyl Alcohol with Water	i, 85
DUPONT (GEORGES). Stereochemical Isomerides of $\Delta\gamma$ -Hexin- β -diol	i, 85
PRILESCHAEFF (NIKOLAUS). Oxidation of Unsaturated Compounds with Organic Superoxides	i, 86
BISTRZYCKI (AUGUSTIN) and AUGUST LANDTWING. Results of Heating the Chlorides of the Higher Fatty Acids	i, 87
FICHTER (FRITZ) and HANS ORLADEN. α -Ethylpentenoic Acids and Xeronic Anhydride	i, 87
FICHTER (FRITZ) and ERWIN GISIGER. β -Methylpentenoic Acids	i, 88
FICHTER (FRITZ), ALBERT KIEFER, and WALTER BERNOULLI. Remarkable Transformation of β -Dialkylated Acrylic Acids when Boiled with Sulphuric Acid	i, 88
FICHTER (FRITZ) and HANS P. LABHAROT. Decomposition of Crotonic Acid by Heating with Ammonia	i, 89
MATZUREVITSH (I.). Synthesis of β -Hydroxy- α -isopropylbutyric Acid	i, 89
STAUDINGER (HERMANN) and ST. BEREZA. Ketens, XIV. Ethyl Ethylketencarboxylate	i, 89
LUNIAK (ANDREAS). Action of Ethyl Bromoacetate and Zinc on the Anhydrides of Monobasic Acids	i, 90
EGOROVA (Mlle. V. I.). Action of Magnesium <i>tert</i> -Butyl Chloride on Ethyl Oxalate	i, 90
VOISENET (E.). Production of Traces of Formaldehyde in the Oxidation of Ethyl Alcohol by Chemical, Physical, or Biological Methods	i, 91
MALVEZIN (PHILIPPE). A New Cupric Salt and its Application as a Fungicide for Diseases of the Vine and other Plants	i, 91
FOURNIER (H.). Catalytic Hydrogenation of Unsaturated Organic Compounds	i, 92
ZEISEL (SIMON) and M. DANIEK. Conversion of <i>isobutyl</i> Alcohol into α -Methylglyceraldehyde	i, 92
BOUYEAULT (LOUIS) and RENE LOCQUIN. Preparation and Description of Condensation Products of Sodium Derivatives of the Acetoins (Hydroxyketones) with Esters of the Acetic Series	i, 92
RUFF (HANS) and SIDONIE KESLER. Effect of Negative Substituents on the Formation of Semicarbazones	i, 93
LÖB (WALTHER) [in part, with G. PULVERMACHER]. Electrolysis of Dextrose, Glycerol, and Glycol	i, 94
LÖB (WALTHER) and GEORG PULVERMACHER. The Fission of Sugars. VII. The Reversal of the Sugar Synthesis	i, 95
VOTOČEK (EMIL) and H. NEMEČEK. Kinetic Studies in the Sugar Series	i, 95
HANRIOT (MAURICE). Chloraloses	i, 95
FOUQUET (G.). The Contraction Occurring when Sucrose is Dissolved in Water	i, 96
SCHOLTZ (MAX). Iron Double Salts of Organic Bases	i, 96
GUTBERG (ALEXANDER) and M. RIESS. Hexahalogen-irideates [Iridichlorides and iridibromides]	i, 97
DAR JUAN (T.). Behaviour of Triethylamine towards Oxidising Agents	i, 98
SCHENCK (MARTIN). Methylated Guanidines	i, 99

	PAGE
SCHENCK (MARTIN). Some Guanidine Derivatives	i, 99
SCHENCK (MARTIN). Glycinamide	i, 100
FISCHER (EMIL) and GEZA ZEMPLÉN. New Synthesis of Amino-hydroxy-acids and of Piperidone Derivatives	i, 100
DAKIN (HENRY D.). Catalytic Action of Amino-acids, Peptones, and Proteins in Effecting Certain Syntheses	i, 101
ROSENHEIM (ARTHUR), ABRAHAM GARFUNKEL, and F. KOHN. Molybdenum Cyanides	i, 101
BÜLOW (CARL) and C. BOZENHARDT. Malonyldihydrazones and their Decomposition Products	i, 102
SMIRNOFF (VLADIMIR A.). Synthesis of Hexahydrocymene [<i>p</i> -Methyl-propylcyclohexane]	i, 104
EARL (JOHN C.). New Space Representation of the Benzene Molecule	i, 104
CHARITSCHOFF (K. W.). Presence of Ethylene Linkings in Benzene and its Homologues	i, 104
GODCHOT (MARCEL). Derivatives of Phenylcyclohexylmethane	i, 104
HOFMANN (KARL A.) and HEINZ KIRMREUTHER [with H. LECHER]. Carbonium Perchlorates	i, 105
BUGUET (ABEL). Cryoscopy of Organic Mixtures and Additive Compounds	i, 105
ROSENMUND (KARL W.). <i>p</i> -Hydroxyphenylethylamine	i, 106
PRZYLUKA (MARIE). Molecular Weights of Liquid Diphenylamine, Triphenylamine, and Aniline Hydrochloride	i, 106
ROSCHDESTVENSKEY (M. S.). Action of Thiocarbimides on Alcohols and Mercaptans. I. New Method for Obtaining Mono-substituted Thio- and Dithio-carbamates of Monoatomic Alcohols and Mercaptans	i, 107
FICHTER (FRITZ) and THEODOR KÜHNEL. 8-Amino-1-naphthol. II.	i, 107
GRISHKEWITSCH-TROCHIMOWSKY (E.). Compounds of Hexamethylene-tetramine with Multivalent Alcohols	i, 108
GRISHKEWITSCH-TROCHIMOWSKY (E.). Tertiary Alcohols of the Tolyllallyl Series	i, 108
TARASOFF (B.). Action of Magnesium on a Mixture of Allyl Bromide and Benzophenone: Synthesis of Diphenylallylcarbinol	i, 109
KUZMIN (W.). Action of Magnesium on a Mixture of Phenyl <i>p</i> -Tolyl Ketone and Allyl Bromide	i, 109
CHARITSCHOFF (K. W.). Structure of Naphthenic Acids	i, 110
HOUBEN (JOSEF) and ROBERT FREUND. Synthesis of Aromatic Amino-Acids. IV. Direct Carboxylation of Dimethylaniline in the Nucleus. Rearrangement of Alkylphenylcarbonates into <i>p</i> - and <i>o</i> -Alkylamino-benzoates	i, 110
EINHORN (ALFRED) and MAXIMILIAN GÜTLER. Benzylaminoacrylic Acids (α -Aminomethylsuccinic Acids)	i, 111
TRÖGER (JULIUS) and H. BREMER. Some Condensation Products from Arylsulphonated Acetonitriles and Aromatic Aldehydes	i, 113
WHEELER (HENRY L.) and CARL O. JOHNS. Halogen-amino-acids. VIII. Position of the Iodine Atoms in Di-iodotyrosine (Iodogorgonic Acid)	i, 114
STORMER (RICHARD). Conversion of Stable Stereoisomeric Ethylene Derivatives into the Labile Modifications by Ultraviolet Light	i, 114
MAUTHNER (FERDINAND). General Synthesis of Phenylated Fatty Acids	i, 115
MOHR (ERNST) and FRIEDRICH KÜHLER. Lactonoid Anhydrides of Acylated Amines. I. The Lactones of Acetylthranoylanthranilic Acid and of Acetylthranilic Acid	i, 116
MOHR (ERNST) [with THEODOR GEIS]. Lactonoid Anhydrides of Acylated Amino-acids. II. Lactone of α -Benzylaminoisobutyric Acid	i, 117
EPSTEIN (FELIX). Condensation of <i>p</i> -Hydroxybenzoic Acid with Formaldehyde	i, 117
BUSCHUEFF (L. V.). New Method of Preparing Ellagic Acid	i, 117
WILLGERODT (CONRAD) and WILHELM HAMBRECHT. Preparation of Acids and Amides from Phenyl Alkyl Ketones by means of Yellow Ammonium Sulphide	i, 117

CONTENTS.

v

	PAGE
REDELIN ² (G.). Preparation of Benzophenoneimine Derivatives	i, 118
STRAUS (FRITZ) [and, in part, A. ACKERMANN and GEORG LUTZ]. Dibenzylideneacetone [Distyryl Ketone] and Triphenylmethane. V. Nature of the Linking of the Halogen Atoms in the Ketohalides of Unsaturated Ketones. I.	i, 119
DELAECHE (MAURICE). The Pyrogenetic Decomposition of (1) β -Benzopinacol and (2) α -Benzopinacol	i, 120
JACKSON (C. LORING) and H. A. FLINT. Action of Acetic Anhydride on Octabromo-1'-hydroxy-1-methoxy-o-quinol-1-monoxide	i, 121
MILLER (OSWALD) and J. SMIRNOFF. Aminoanilide and Certain New Dianilides of α -Naphthaquinone	i, 121
BUSCHUEFF (L. V.). Action of Piperidine on <i>d</i> -Pinene Chloro-oxime	i, 122
ANWERS (KARL). Conversion of Pulegone into Menthones	i, 122
THOM (HERMANN). Matiao Leaves and Matiao Oils	i, 122
ENKLAAR (C. J.). The Essential Oil of Hyacinths	i, 122
FEIST (KARL). Decomposition of Amygdalin	i, 123
LÖWY (EMIL). Crystalline Chitosan Sulphate	i, 123
NIERENSTEIN (MAXIMILIAN) and T. A. WEBSTER. Formation of Phloba- pheus	i, 124
HENZOG (JOHANNES) and D. KROHN. Constituents of the Rhizome of <i>Imperatoria</i>	i, 124
OESTERLE (OTTO A.) and G. RIAT. Rhein	i, 126
WILLSTÄTTER (RICHARD) and HERMANN FRITZSCHE. Chlorophyll. VIII. Degradation of Chlorophyll by Alkalis	i, 126
SCHROEDER (JOHANN VON). The Tanning Process	i, 129
BLANKSMA (JAN J.). Constitution of Hydroxymethylfurfuraldehyde	i, 130
KALUZA (LUDWIG). Substituted Rhodanic Acids and their Aldehyde Con- densation Products. VIII.	i, 130
EINHORN (ALFRED) and MAXIMILIAN GÜTTLER. Additive Products of Halogen Acetamide with Atropine	i, 131
ULTÉE (A. J.). Caffeine	i, 132
FRERUND (MARTIN) and FRITZ MAYER. Action of Grignard's Solutions on β -Cinchonine- and β -Quinine-ethiodides	i, 132
PLANCHER (GIUSEPPE) and U. PONTI. Action of Chloroform on 2:5-Di- methylpyrrole	i, 132
PILOTY (OSCAR) and E. QUITMANN. Constitution of Hemopyrrole and of Hemopyrrolecarboxylic Acid	i, 133
SCHIFF (ROBERT). New Cinchonic Acid Syntheses	i, 134
EINHORN (ALFRED) [with RICHARD FEIBELMANN and MAXIMILIAN GÜTTLER]. Quinoline Derivatives	i, 134
WAHL (ANDRÉ) and ANDRÉ MEYER. Action of Magnesium cyclohexyl- bromide on Tetramethyldiaminobenzophenone	i, 134
WILLSTÄTTER (RICHARD) and ARTHUR STOLL. Reaction of Nitrosoamides with Phenylhydrazine	i, 134
PADOA (MATRICE) and F. GRAZIANI. New Phototropic Substances. II.	i, 135
FISCHER (EMIL) and ANDREAS LUNAK. Synthesis of Polypeptides. XXXII. Derivatives of <i>l</i> -Proline and of Phenylalanine	i, 136
KOHN (MORITZ) and FRIEDRICH BUM. Aminopyrrolidone Derivatives from Mesityloxide and Aminolactones from Diacetone Alcohol	i, 136
EINHORN (ALFRED) and MAXIMILIAN GÜTTLER. Action of Formaldehyde and Secondary Bases on Isatin	i, 137
DANAILA (NEGOITA). Synthesis of 5:7:5':7'-Tetrabromoindigotin and 5:7:5':7'-Tetrachloroindigotin	i, 137
MAILLARD (LOUIS C.). Constitution of Indirubin	i, 138
FRUNDLER (PAUL). 1-Hydroxyindazol Derivatives	i, 138
WHEELER (HENRY L.) and DAVID F. McFARLAND [and, in part, WALTER F. STOREY]. Pyrimidines. XLIX. Thio-derivatives of Thymine and the Preparation of Thymine	i, 138
FRANCHIMONT (ANTOINE P. N.) and E. KRAMER. Derivatives of Piper- azine	i, 139

	PAGE
ZINCKE (THEODOR) and E. SCHARFF. Ketochlorides and Quinones of Heterocyclic Compounds and Their Transformation-Products. III. Ketochlorides and Quinones of Phenyl-4-aziminobenzene [2:1:3-Benzotriazole]	i, 140
BUSCH (MAX), J. REINHARDT, and O. LIMPACH. Isomeric Thionrazoles	i, 142
ZEREWITINOFF (TH.). Organic Salts of Violuric Acid	i, 143
LEYKO (Z.) and LEON MARCILEWSKI. Hamopyrrole. II.	i, 144
BUCHERER (HANS TH.) and ERNST F. SONNENBURG. Action of Sulphites on Atomic Amino- and Hydroxyl Compounds. VIII. Behaviour of Hydrazines, especially of Phenylhydrazine, in the Sulphite Reaction	i, 144
SCALA (ALBERTO) and GIUSEPPE BONAMARTINI. Compounds of Copper with Egg-Albumin	i, 146
MANDEL (JOHN A.). The Scission Products of the Nucleo-protein of Milk Glands	i, 147
SÖRENSEN (SØREN P. L.). Studies on Enzymes. II. Measurement and Meaning of the Concentration of the Hydrogen Ions in Enzymatic Processes	i, 147
GRAFE (VICTOR). [The Enzymes of Gum-acacia and certain other Gums]	i, 148
FARBWERKE FORM. MEISTER, LUCIUS and BRÜNING. Preparation of Hydroxyarylarsonic Oxides	i, 148
BENDA (LUDWIG). <i>o</i> -Aminoarylarsonic Acids	i, 148
FARBWERKE FORM. MEISTER, LUCIUS and BRÜNING. Preparation of Carbamide and of Thiocarbamide Derivatives of <i>p</i> -Aminophenylarsonic Acids	i, 148

PART II.

General and Physical Chemistry.

CUTHERBERTSON (CLIVE) and MAUDE CUTHERBERTSON. Refraction and Dispersion of Air, Oxygen, Nitrogen, and Hydrogen and their Relations	ii, 85
CUTHERBERTSON (CLIVE) and MAUDE CUTHERBERTSON. Refraction and Dispersion of Sulphur Dioxide and Hydrogen Sulphide and their Relation to those of their Constituents	ii, 85
CUTHERBERTSON (CLIVE) and MAUDE CUTHERBERTSON. Refraction and Dispersion of Neon	ii, 85
GRAMONT (ANTOINE DE). Distribution of the Ultimate Rays in the Spectrum of Different Regions of the Sun	ii, 85
HICKS (WILLIAM M.). Critical Study of Spectral Series. I. The Alkalies, Hydrogen and Helium	ii, 86
HEMSALECH (GUSTAVE A.) and CHARLES DE WATTEVILLE. Line Spectrum of Calcium given by the Oxy-acetylene Burner	ii, 86
HEMSALECH (GUSTAVE A.) and CHARLES DE WATTEVILLE. The Yellow, Orange, and Red Regions of the High Temperature Flame Spectrum of Calcium	ii, 86
ROYDS (T.). Series Systems in the Spectra of Zinc, Cadmium, and Mercury	ii, 87
KRETZER (A.). The Spectrum of Antimony	ii, 87
BEVAN (P. V.). Absorption Spectrum of Potassium Vapour	ii, 87
JONES (HARRY C.) and W. W. STRONG. Absorption Spectra of Various Salts in Solution, and the Effect of Temperature on Such Spectra. XXVI.	ii, 87
BRÜNINGHAUS (L.). A Relation between Absorption and Phosphorescence	ii, 88
BRÜNINGHAUS (L.). Theory of the Law of the Optimum of Phosphorescence	ii, 89
RASSENFOSSER (A.). Electrolytic Conductivity of Fluorescent Solutions	ii, 89
POCHETTINO (ALFREDO). Luminescence of Crystals	ii, 89

CONTENTS.

vii

	PAGE
POHL (ROBERT). Dependence of the Photo-electric Effect of the Alkali Metals in Polarised Light on the Wave-length.	ii, 90
TRIVELLI (A. P. H.). Theory of the Ripening Process of the Silver Haloids	ii, 90
BROCHET (ANDRÉ). New Determinations of the Radioactivity of the Thermal Waters of Plombières	ii, 90
MAKOWER (WALTER) and SIDNEY RUSS. The Recoil of Radium-C from Radium-B.	ii, 91
KOLOWRAT (L.). Disengagement of Emanation from Radium Salts.	ii, 91
KLEEMAN (R. D.). Nature of the Ionisation of a Molecule by an α -Particle	ii, 92
GRIGER (H.) and E. MARSDEN. The Number of α -Particles Expelled from the Actinium and Thorium Emanations	ii, 92
ROBINSON (JAMES). The Absorption of Cathode Rays of Different Velocity in Helium	ii, 93
GRUMBACH (ALBERT). Contact Electrification	ii, 93
DOBROSERDOFF (DIMITRI K.). Dielectric Properties of the Elements	ii, 93
DOBROSERDOFF (DIMITRI K.). Quantitative Relations between the Dielectric Constants and other Properties of Substances	ii, 94
GARDNER (J. A.). The Conductivity of Mixtures of Dilute Solutions	ii, 95
BRON (EUGEN VON) and B. P. APHANASSIEFF. Cadmium Chloride Concentration Cells	ii, 95
JUST (GERHARD), PAUL ASKENASY, and B. MITROFANOFF. Rapid Formation of Positive Lead Accumulator Plates	ii, 96
KOHLSCÜTTER (VOLKMAR). Volatilisation of Cathodes. VI.	ii, 96
SPENCER (JAMES F.) and MARGARET LE PLA. Electrode for Determining the Concentration of the CO_3^{2-} Ion and the Condition of Silver Carbonate in Solution	ii, 97
KOSSONOGOFF (J. J.). Investigation of Electrolysis with the Ultra-microscope	ii, 97
FICHTER (FRITZ) and HANS KAPPELER. Electrolytic Oxidation of Ammonium Carbonate	ii, 98
ALEXÉEFF (D.). Electro-catalysis	ii, 98
HEUSLER (FRIEDRICH) and FRANZ RICHARZ. Manganese, Aluminium, and Copper	ii, 99
MESLIN (GEORGES). Magnetic Dichroism of Siderite in Liquids	ii, 99
DRAPIER (PAUL). Magnetism of Solutions	ii, 99
PASCAL (PAUL). Use of the Magnetic Field as a means of Determining Constitution in Organic Chemistry. II. and III.	ii, 100
GLASER (ERHARD). Thermometers as Thermo-regulators	ii, 101
RECHENBERG (C. VON). Kraft's Boiling point Estimations and his Theory of Volatilisation	ii, 101
GABASKIN (D. D.) and A. E. MAKOVETZKI. Preparation of a Mixture of Constant Boiling-point and Maximum Vapour Pressure by Distillation	ii, 101
MAKOVETZKI (A. E.). Determination of the Composition of Constant Boiling-point Mixtures having Maximum Vapour Pressures and their Quantitative Separation by Distillation	ii, 101
SWIETOSLAWSKI (W.). An Electrical Apparatus for the Direct Determination of the Water Value of a Calorimeter	ii, 102
COHEN (ERNST) and J. OLIE, jun. Atomic Volume of Allotropic Modifications at Very Low Temperatures	ii, 102
KURBATOFF (W. A.) and G. G. ELISEEFF. Associated Liquids	ii, 102
ELISEEFF (G. G.) and W. A. KURBATOFF. Association of Glycerol	ii, 103
BOURNAT (Y.). Adsorption of Ions	ii, 103
ROHLAND (PAUL). Adsorptive Power of Hydroxides of Silicon, Aluminium, and Iron. III. Adsorption by Clay. II.	ii, 104
REYCHLER (ALBERT). Chemical Dynamics and the Colloidal State. I, II, and III.	ii, 104
BILTZ (WILHELM). Adsorption of Arsenious Acid by Ferric Hydroxide	ii, 106

	PAGE
BAKKER (GERRIT). Thermodynamics of the Capillary Layer	ii, 106
HEYDWEILLER (ADOLF). Relationship between Physical Properties of Solutions. I. Density and Electrical Conductivity of Aqueous Solutions of Salts	ii, 106
GUGLIEMMO (GIOVANNI). Condition of Equilibrium between a Dilute Solution and the Pure Solvent Separated by a Semi-permeable Diaphragm or by the Vapour of the Solvent	ii, 107
PATTERSON (THOMAS S.). Binary Mixtures and Concentrated Solutions. Remarks on Dolezalek's Paper	ii, 107
SVEDBERG (THE). Existence and Properties of Disperse Systems in the Region Separating Colloidal and Crystalloidal Solutions	ii, 108
DUCLAUX (JACQUES). Theory of Colloids	ii, 108
DETCKER (KARL). General Equation of State	ii, 110
BOULOUGH (R.). Demonstration of the Phase Rule	ii, 110
GORBOFF (ALEX). Invariant Systems and the Regularity of Composition of Certain Eutectics	ii, 111
DUMANSKY (A. V.). Influence of Centrifugal Force on the Equilibrium of Chemical Systems	ii, 112
BRÖNSTED (J. N.). Chemical Affinity. III. Solution-affinity of Binary Systems. II. Sulphuric Acid and Water	ii, 112
MÜLLER (PAUL TH.). Affinity of Sodium Phosphate for Water	ii, 113
SACKUR (OTTO). Chemical Kinetics	ii, 113
TRAUTZ (MAX). Temperature-coefficient of Chemical Reaction Velocities. IV. Addendum	ii, 114
PETERS (WALTER). Residual Affinity and Additivity. Part II.	ii, 114
WINTHEE (CHR.). Eder's Solution. I.	ii, 115
GUYR (PHILIPPE A.) and N. ZACHARIADIS. Vacuum Correction of Weighings Applied to Atomic Weight Determinations	ii, 116
SUTHERLAND (WILLIAM). The Fundamental Constant of Atomic Vibration and the Nature of Dielectric Capacity	ii, 116
SUTHERLAND (WILLIAM). Molecular Diameters	ii, 116
SAIKI (TADASU). Liquid Extraction with the Aid of Soxhlet's Apparatus	ii, 117
GIRDWOOD (GILBERT P.). Apparatus for Evaporating Ethereal Solutions	ii, 117

Inorganic Chemistry.

WAERTIG (PERCY). Condition of Dissolved Iodine	ii, 114
AUBEL (EDMUND VAN). Production of Ozone by Ultraviolet Light	ii, 118
PREUNER (GERHARD) and W. SCHUPP. Dissociation Isotherms of Sulphur between 300° and 350°	ii, 118
PÉLABON (HENRI). Action of Hydrogen on Sulphur or Selenium in Presence of Another Element	ii, 118
POCHETTINO (ALFREDO). Preparation of Colloidal Solutions of Selenium	ii, 119
BRINKER (E.) and A. WROCZYŃSKI. Chemical Reactions in Gases Submitted to Very High Pressures; Decomposition of Nitric Oxide; Formation of Nitrosyl Chloride	ii, 120
BESSON (ADOLPHE) and A. FOURNIER. A New Chloride of Phosphorus	ii, 121
STOCK (ALFRED). Phosphorus Suboxide	ii, 121
CORNEO (E.). Formula of Hypophosphoric Acid. I. and II.	ii, 121
JORISSEN (WILLEM P.) and N. H. SIEWERTSZ VAN REESEMA. Extinction of Flames	ii, 122
HABER (FRITZ) and BURRITT S. LACY. Inner Cone of the Bunsen Flame	ii, 122
WEISS (LUDWIG) and THEODOR ENGELHARDT. Nitrogen Compounds of Silicon	ii, 122
LE BLANC (MAX) and L. BEGMANN. Action of Metals on Fused Sodium Hydroxide	ii, 123
FORCAND (ROBERT DE). Alkali Hydrogen Carbonates	ii, 124

CONTENTS.

ix

	PAGE
FORCRAND (ROBERT DE). Hydrates of Rubidium and Cæsium Hydroxides	ii, 124
D'ANS (JOHANN). Acid Sulphates . V.	ii, 125
BAUBIGNY (HENRI). Action of Heat and Light on Silver Sulphite and its Alkali Double Sulphites. Amount of Dithionate Obtained	ii, 125
BAUBIGNY (HENRI). Necessity for Exactness in Describing Reactions. [Action of Heat on Sulphites]	ii, 125
ROHLAND (PAUL). New Preparation of the Second Anhydrous Modification of Calcium Sulphate	ii, 125
RIESENFIELD (ERNST H.). Decomposition of Calcium Carbonate	ii, 126
DORP (G. C. A. VAN) and J. RODENBURG. Solubility of Cadmium Sulphide in Light Petroleum Containing Oil	ii, 126
SPRING (WALTHER). [Formation of Alloys by Pressure]	ii, 126
GUERTLER (W.). Constitution and Heat Contents of Lead-Tin Alloys	ii, 126
MARINO (LUIGI). Peroxidised Compounds	ii, 126
TUTTON (ALFRED E. H.). Relation of Thallium to the Alkali Metals: a Study of Thallium Zinc Sulphate and Selenate	ii, 127
D'ANS (JOH.) and O. FRITSCHER. Acid Sulphates. VI.	ii, 127
JONKER (W. P. A.). The System Mercuric Chloride and Mercurous Chloride	ii, 127
WELSBACH (CARL AUGER VON). Resolution of Ytterbium	ii, 128
BRONIEWSKI (WITOLD). Electrical Properties of Aluminium Copper Alloys	ii, 128
ROSENHAIN (WALTER) and J. C. W. HUMFREV. Crystalline Structure of Iron at High Temperatures	ii, 128
KRASSA (F.). Passivity of Iron	ii, 129
ROHLAND (PAUL). Retardation of the Oxidation of Iron by Chromic Chloride	ii, 129
GOUTAL (E.). Carbon Monoxide in Steels	ii, 129
HILFERT (SIGGFRIED). Oxygen Evolved from Ferric Oxide at High Temperatures	ii, 130
KONSTANINOFF (N. S.). Phosphorus Compounds of Iron	ii, 130
KUHN (OTTO). Iron Phosphides	ii, 131
DUCELLIEZ (F.). Electromotive Forces of Cobalt Alloys	ii, 131
LAMBRI (GUSTAV). Absorption of Carbon by Metals, Especially Nickel, in the Electrolysis of Aqueous Solutions	ii, 131
VIGOUROUX (EMILE). Alloys of Nickel and Copper	ii, 132
JOLIBOIS (PIERRE). Two New Nickel Phosphides	ii, 132
AUGER (VICTOR). Mixed Halogen Compounds of Tin	ii, 133
WEISS (LUDWIG) [and, in part, RICHARD LEHMANN]. Natural Zirconium Dioxide	ii, 133
WARTENBERG (H. VON). Thorium	ii, 134
PRANDTL (WILHELM) and BENNO BLEYER. The Atomic Weight of Vanadium	ii, 134
DELÉFINE (MARCEL). Solution of Platinum in Sulphuric Acid and the Products of Reaction	ii, 135

Mineralogical Chemistry.

BRUN (ALBERT). Volcanic Gases	ii, 135
MOUREU (CHARLES) and A. LEPAPE. Gas from Thermal Springs: Presence of Krypton and Xenon	ii, 136
GRAHAM (RICHARD P. D.). Dawsonite, a Sodium-Aluminium Carbonate	ii, 136
TSCHEERNIK (G. P.). Chemical Investigation of a Uranium Mineral from Borneo	ii, 136
VERNADSKY (VLADIMIR I.). Isomerism in the Group of Alumino- and Ferri-silicates	ii, 136

Physiological Chemistry.

	PAGE
HENDERSON (YANDELL). Acapnia and Shock. IV. Fatal Apnoea after Excessive Respiration	ii, 137
MANCHOT (WILHELM) [and, in part, W. BRANDT] Union of Oxygen in Blood	ii, 137
COHNHEIM (OTTO), KREGLINGER and KREGLINGER. Physiology of Water and Sodium Chloride	ii, 133
HENDERSON (LAWRENCE J.). Neutrality Equilibrium in Blood and Protoplasm	ii, 139
BUGLIA (GIUSEPPE) and L. KARCZAG. Influence of Stereochemical Configuration on Certain Physico-chemical Properties of Organic Colloids	ii, 139
COLLINGWOOD (BRETRAM J.). Reversed Activity of Tissue Extract made at High Temperatures	ii, 139
MICHAELIS (LEONOR) and PETER RONA. Glycolysis. I. The Susceptibility to Alkali of Dextrose	ii, 139
GUDZENT (F.). Physico-chemical Behaviour of Uric Acid and its Salts in the Blood	ii, 140
KAWASHIMA (K.). The Behaviour of the Anti-Substances of the Blood-Serum Towards Solvents and Other Reagents	ii, 140
MIGAY (TH. J.) and W. W. SAWITSON. The Proportionality of Proteolytic and Rennetic Action of the Gastric Juice of Man and Dog in Normal and Pathological Cases	ii, 140
GAUTRELET (ÉMILE). Partial Transformation of Alimentary Fatty Matter into Mannitols by Peptic and Pancreatic Digestion in vitro	ii, 140
CHOAY (EUGÈNE). Action of Heat on Dry Pancreatic Extract	ii, 141
TERRONIS (ÉMILE F.). Fat Cleavage by Pancreatic Juice. I.	ii, 141
GREER (J. R.) and F. C. BECHT. Concentration of Anti-substances in the Body-Fluids of Normal and Immune Animals	ii, 141
THAR (H.). The Purine Bases of the Bone-marrow	ii, 141
VANDEVELDE (ALBERT J. J.). The Sugar Destructions in Animal Organisms which are Measurable by the Polarimeter	ii, 141
SAIKI (TADASU). Lactic Acid in the Autolysed Dog's Liver	ii, 142
TRUFFI (MARCO). The Action of Mercury Salts on Autolysis	ii, 142
SALKOWSKI (ERNST). Cholesterol Esters in the Human Epidermis and their Reactions	ii, 142
MACLEAN (HUGH) and OWEN T. WILLIAMS. The So-called Fat of Tissues and Organs	ii, 142
KOCH (WALDEMAR). The Importance of Phosphatides for the Living Cell. II.	ii, 142
MACLEAN (HUGH). The Relationship of Diastatic Efficiency to Average Glycogen Content in Tissues and Organs	ii, 142
BOTTAZZI (FILIPPO) and NOÉ SCALINCI. Chemico-physical Investigations on the Crystalline Lens	ii, 143
WHEELER (HENRY L.) and LAFAYETTE B. MENDEL. The Iodine Complex in Sponges	ii, 143
EPSTEIN (ALBERT A.). The Theory of Urea Formation	ii, 143
PORCHER (CH.). The Origin of Lactose	ii, 144
BALDWIN (HELEN). Influence of Lactic Acid Ferments on Intestinal Putrefaction in a Healthy Individual	ii, 144
MACLEOD (JOHN J. R.) and R. G. PEARCE. Experimental Glycosuria. V. The Distribution of Glycogenolytic Ferment in the Animal Body, especially of the Dog	ii, 144
DAKIN (HENRY D.). The Urorosein Reaction	ii, 145
HERTZ (ARTHUR F.), F. COOK, and E. G. SCHLESINGER. The Action of Saline Purgatives	ii, 145
URY (HANS). The Estimation of Ferments in the Forces	ii, 145
SAIKI (TADASU). Chemistry of Cancer. II. Purine Bases, Creatine, and Creatinine	ii, 146

CONTENTS.

xi

	PAGE
HOCKENDORF (PAUL). The Influence of Certain Alcohols, Hydroxy- and Amino-acids of the Aliphatic Series on the Sugar and Nitrogen Excretion in Phloridzin Diabetes of the Dog. I.	ii, 146
ERLANDSEN (A.). Phloridzin Diabetes. I.	ii, 146
GUDZENT (F.). Gout	ii, 146
SIEDER (NADINE). The Influence of Alcohol on the Quantity of Phosphatides in Animal Organs	ii, 147
LOEB (JACQUES). The Chemical Constitution and Physiological Action of Alcohols and Acids. II.	ii, 147
KOWALEWSKY (KATHARINA). The Fate of Histidine in the Body of the Dog	ii, 147

Chemistry of Vegetable Physiology and Agriculture.

HERTER (CHRISTIAN A.). Action of Sodium Benzoate on the Multiplication and Production of Gas by Various Bacteria	ii, 147
SEVERIN (S. A.). Decomposition of Nitrates by Bacteria	ii, 148
POZZI-ESCOR (M. EMMANUEL). Alcoholic Fermentation in the Presence of Sulphurous Acid	ii, 148
KOSTYTSHEFF (S.). The Influence of Fermented Sugar Solutions on the Respiration of Wheat Seedlings	ii, 148
ZALESKI (W.) and A. REINHARD. The Influence of Mineral Salts on the Respiration of Germinating Seeds	ii, 148
ZALESKI (W.). The Part Played by Oxygen in the Formation of Protein in Plants	ii, 149
PANTANELLI (ENRICO) and M. SELLA. Selective Absorption of Ions by Roots	ii, 149
HÉBERT (ALEXANDRE) and GEORGES TRUFFAUT. Nitrogenous and Mineral Composition of Ornamental Plants	ii, 150
WILLSTÄTTER (RICHARD), FERDINAND HOCHBERG, and ERNST HUG. Chlorophyll. VII. Comparative Investigation of the Chlorophyll of Different Plants	ii, 150
PÉRROT (EM.) and M. LEPRINCE. <i>Adenium Hongkoi</i> , the Ordeal Poison of the French Soudan	ii, 151
KHOURI (JOSEPH). Presence of a Glucoside, which is Decomposed by Emulsin, in the Leaves and Twigs of <i>Ercnostachys lacinata</i>	ii, 151
MALVEZIN (PHILIPPE). A New Cupric Salt and its Application as a Fungicide for Diseases of the Vine and other Plants	ii, 151
MALVEZIN (PHILIPPE). Oxidation Taking Place in Wines	ii, 151
HUBERT. Disappearance of Sulphur Dioxide	ii, 152
ANDRIK (KARL), V. BARTOS, and J. UHRMAN. Difference of Races and Individual Beets with Regard to their Composition	ii, 152

Analytical Chemistry.

EMICH (FRIEDRICH) and JULIUS DONAU. Manipulation of Small Precipitates. Qualitative and Quantitative Micro-chemical Analysis	ii, 152
EISENSTEIN (ALFRED) and FRIEDRICH ZIEFFER. Apparatus for Filtering at a Constant Temperature	ii, 153
MICHAELIS (LEONOR) and PETER ROSA. The Influence of Neutral Salts on Indicators	ii, 153
POZZI-ESCOR (M. EMMANUEL). A New Sensitive Indicator. Dimethyl-Brown	ii, 153
MILORENDSKI (THADDEUS). Systematic Detection of the More Important Acids	ii, 154
CRONHEIM (WALTER). The Detection of Hydrofluoric Acid in Presence of Fluorides	ii, 154

	PAGE
MULLER (JOSEPH A.). Action of Iodine on Sodium Dithionate or Trithionate in Solution	ii, 154
MARINO (LUIGI). Volumetric Estimation of Selenious Acid in Alkaline Solution by Permanganate	ii, 155
HUGUET. Estimation of Total Nitrogen in Urine	ii, 155
BARRAL (ÉTIENNE). Source of Error in Estimating Ammonia	ii, 155
POZZI-ESCOOT (M. EMMANUEL). Estimation of Nitrogen in Nitrates by Reduction with the System Aluminium-Mercury	ii, 155
LUTZ (OSCAR) and R. SVINNE. Detection of Arsenic Acid in Presence of Arsenious Acid by means of Magnesia Mixture	ii, 156
GAUVRY (E.). Detection of Boric Acid in Butter and Milk	ii, 156
LISSNER (A.). Ultimate Analysis of Coals Containing [Hydrated] Clays	ii, 156
GOUTAL (E.). Estimation of Carbon Monoxide in Air	ii, 157
GOUTAL (E.). [Estimation of Carbon] Monoxide in Steels	ii, 157
TANANAEFF (N.) and D. TSUKERMAN. Titration by means of Borax in Presence of Glycerol	ii, 158
TAYLOR (JAMES M.). Estimation of Zinc in the Presence of Iron	ii, 158
SANCHEZ (JEAN A.). New Volumetric Method for the Estimation of Copper	ii, 158
SACHER (JULIUS F.). Volumetric Estimation of Lead with Alkaline Permanganate	ii, 158
BROWNING (PHILIP E.) and EDWIN J. ROBERTS. Substitution of Bromine and of Iodine for Chlorine in the Separation of Cerium from the other Cerium Earths	ii, 159
MULLER (JOSEPH A.). Estimation of Chromium in Chrome Iron Ore	ii, 159
WOLTER (LUDWIG). Estimation of Tungsten in Tungsten-Steel	ii, 160
POZZI-ESCOOT (M. EMMANUEL). Separation of Vanadium, Molybdenum, Chromium, and Nickel in Special Steels	ii, 160
SANGER (CHARLES R.) and ÉMIL RAYMOND RIEGEL. Estimation of Antimony by Gutzeit's Method	ii, 161
CHESNEAU (GABRIEL). Analysis of Columbites and Tantallites	ii, 161
SIDERSKY (D.). Process for the Rapid Estimation of Alcohol	ii, 161
STOECKLIN (E. DE). New Method for Detecting Traces of Alcohols	ii, 162
VOLCY-BOUCHER and J. GIRAUD. Detection of Resorcinol by means of the Cyano-cupric Reaction	ii, 162
NECKING (JOSEPH). The Methods of Lecithin Estimation	ii, 162
RUPP (ERWIN) and F. LEHMANN. Volumetric Estimation of Sugars by K. Lehmann's Process	ii, 163
MARGAILLAN (L.). Separation of Sucrose and Lactose by the Bulgarian Ferment	ii, 162
BANG (IVAR) and GÖSTA BOHMANNSSON. The Method of Estimating Sugar in Urine	ii, 163
GRIMBERT (LÉON) and R. BERNIER. Camidge's Reaction	ii, 163
REICHARD (C. J.). Detection of Reducing Substances in Urine	ii, 163
FREY (WALTHER) and ALFRED GIGON. The Quantitative Estimation of Amino-acids in Urine by means of Formaldehyde Titration	ii, 164
HENRIQUES (VALDEMAR) and SÖREN P. L. SÖRENSEN. The Quantitative Estimation of Amino-acids, Polypeptides, and Hippuric Acid in Urine by means of Formaldehyde Titration	ii, 164
YOSHIDA (TANYO). The Formaldehyde Titration of Amino-acids in Urine	ii, 164
JOLLES (ADOLF). Detection of Biliary Acids, Lævulose, Glyconic Acid, and Pentoses in Urine	ii, 164
FRITSCH (RODOLFO). Detection of Biliary Acids [and Acetone]	ii, 165
TÓTH (JULIUS). Thiocyanates in Tobacco Smoke	ii, 165
MALAQUIN (PAUL). New Test for Strychnine	ii, 165
PROCNOW (A.). Estimation of the Xanthine Bases in Cocoa and Chocolate	ii, 165
BENEDICT (STANLEY R.) and TADASU SAIKI. Estimation of Purine Nitrogen in Urine	ii, 166
SATO (T.). New Reactions of Thiocarbamide	ii, 166
SABAKI (TAKAKI). A New and Sensitive Reaction of Scatole	ii, 166

CONTENTS.

xiii

	PAGE
TESTONI (GIUSEPPE). Estimation of "Saccharin" [o-Benzolsulphinide] in Various Foods	ii, 167
VAN DORP (G. C. A.) and J. RODENBURG. Estimation of Tannin [in Catechu]	ii, 167
SCHUMM (OTTO). The Detection of Blood-pigment by its Absorption of the Violet End of the Spectrum	ii, 167
HATA (S.). The Estimation of Pepsin by the Clarification of a Turbid Solution of Egg-white	ii, 168
BRUNN (JULIUS). Employment of the Guaiacol Method for the Quantitative Estimation of Peroxydase	ii, 168
LÖWY (M). A Test for Mushrooms	ii, 168

INDEX OF AUTHORS' NAMES

IN TRANSACTIONS AND ABSTRACTS

A.

Ackermann, A. See F. Straus.
 Alexéeff, D., ii, 99.
 Andriik, K., V. Bartoš, and J. Urban, ii, 152.
 Aphanassieff, B. P. See E. von Biron.
 Askenasy, P. See G. Just.
 Aubel, E. van, ii, 118.
 Auger, V., ii, 133.
 Aurers, K., i, 122.

B.

Bakker, G., ii, 106.
 Baldwin, H., ii, 144.
 Bang, I., and G. Bohmannsson, ii, 163.
 Barger, G., and A. J. Ewins, TRANS., 284.
 Barnett, E. de B., and S. Smiles, TRANS., 186.
 Barral, E., ii, 155.
 Bartoš, V. See K. Andriik.
 Baubigny, H., ii, 125.
 Becht, F. C. See J. R. Greer.
 Benda, L., i, 148.
 Benedict, S. R., and T. Saiki, ii, 166.
 Bereza, S. See H. Staudinger.
 Bergmann, L. See M. Le Blanc.
 Bernier, R. See L. Grimbart.
 Bernoulli, W. See F. Fichter.
 Berry, A. J., TRANS., 196.
 Besson, A., and A. Fournier, ii, 121.
 Bevan, P. V., ii, 87.
 Biltz, W., ii, 106.
 Biron, E. von, and B. P. Aphanassieff, ii, 95.
 Bistrzycki, A., and A. Landtwing, i, 87.
 Blanksma, J. J., i, 130.
 Bleyer, B. See W. Prandtl.
 Bohmannsson, G. See I. Bang.

Bonamartini, G. See A. Scala.
 Bottazzi, F., and N. Scalinai, ii, 143.
 Boulouch, R., ii, 110.
 Bournat, V., ii, 103.
 Bouveault, L., and R. Loequin, i, 92.
 Boyle, Miss M., TRANS., 211.
 Bozenhardt, C. See C. Bülow.
 Brandt, W. See W. Manchot.
 Bremer, H. See J. Tröger.
 Briner, E., and A. Wroczynski, ii, 120.
 Brochet, A., ii, 90.
 Brönsted, J. N., ii, 112.
 Broniewski, W., ii, 128.
 Brownings, F. E., and E. J. Roberts, ii, 159.
 Brüninghaus, L., ii, 88, 89.
 Brun, A., ii, 135.
 Brunn, J., ii, 163.
 Bucherer, H. T., and E. F. Sonnenburg, i, 144.
 Bülow, C., and C. Bozenhardt, i, 102.
 Buglia, G., and L. Karczag, ii, 139.
 Buguet, A., i, 105.
 Bum, F. See M. Kohn.
 Busch, M., O. Limpach, and J. Reinkardt, i, 142.
 Buschneff, L. V., i, 117, 122.

C.

Challenger, F., and F. S. Kipping, TRANS., 142.
 Chaney, N. K. See F. D. Chattaway.
 Charitschkoff, K. W., i, 104, 110.
 Chattaway, F. D., and N. K. Chaney, TRANS., 292.
 Chesneau, G., ii, 161.
 Choay, E., ii, 141.
 Cohen, E., and J. Olie, jun., ii, 102.
 Cohnhelm, O., Kreglinger and Kreglinger, ii, 138.

Collingwood, B. J., ii, 139.
Cook, F. See A. F. Hertz.
Cornec, E., ii, 121.
Cronheim, W., ii, 164.
Crossley, A. W., and Miss G. H. Wren, *TRANS.*, 98.
Cuthbertson, C., and M. Cuthbertson, ii, 85.
Cuthbertson, M. See C. Cuthbertson.

D.

Dakin, H. D., i, 101; ii, 145.
Danaila, N., i, 137.
Daniek, M. See S. Zeisel.
D'Ans, J., ii, 125.
D'Ans, J., and O. Fritsche, ii, 127.
Dar Juan, T., i, 98.
Deleare, M., i, 120.
Delcpine, M., ii, 135.
Dobroserdoff, D. K., ii, 93, 94.
Donau, J. See F. Emich.
Dorochewsky, A. G., and M. S. Roschdestvensky, i, 85.
Dorp, G. C. A. van, and J. Rodenburg, ii, 126, 167.
Drapiet, P., ii, 99.
Drucker, K., ii, 110.
Ducelliez, F., ii, 131.
Duclaux, J., ii, 108.
Dumansky, A. V., ii, 112.
Dupont, G., i, 83.

E.

Earl, J. C., i, 104.
Edminton, S. R., and T. P. Hilditch, *TRANS.*, 223.
Egorova, Mlle. V. I., i, 90.
Einhorn, A., R. Feibelman, and M. Göttler, i, 134.
Einhorn, A., and M. Göttler, i, 111, 131, 137.
Eisenstein, A., and F. Ziffer, ii, 153.
Elisécff, G. G., and W. A. Kurbatoff, ii, 103.
Elisécff, G. G. See also W. A. Kurbatoff.
Emich, F., and J. Donau, ii, 152.
Engelhardt, T. See L. Weiss.
Enklaar, C. J., i, 122.
Epstein, A. A., ii, 143.
Epstein, F., i, 117.
Erlandsen, A., ii, 146.
Ewins, A. J. See G. Barger.

F.

Farbwerke vorm. Meister, Lucius & Brüning, i, 148.

Feibelman, R. See A. Einhorn.
Feist, K., i, 123.
Fichter, F., and E. Gisiger, i, 88.
Fichter, F., and H. Kappeler, ii, 98.
Fichter, F., W. Bernoulli, and A. Kiefer, i, 88.
Fichter, F., and T. Kühnel, i, 107.
Fichter, F., and H. P. Labhardt, i, 89.
Fichter, F., and H. Obladen, i, 87.
Fischer, E., and A. Luniak, i, 136.
Fischer, E., and G. Zemplén, i, 100.
Flint, H. A. See C. L. Jackson.
Forcrand, R. de, ii, 124.
Forster, M. O., and Miss H. M. Judd, *TRANS.*, 254.
Forster, M. O., and R. Müller, *TRANS.*, 126.
Fouquet, G., i, 96.
Fournier, A. See A. Besson.
Fournier, H., i, 92.
Franchimont, A. P. N., and E. Kramer, i, 138.
Frankland, P. F., and D. F. Twiss, *TRANS.*, 154.
Freund, M., and F. Mayer, i, 132.
Freund, R. See J. Houben.
Freundler, P., i, 133.
Frey, W., and A. Gigon, ii, 164.
Fritsch, R., ii, 165.
Fritsche, O. See J. D'Ans.
Fritzsche, H. See R. Willstätter.

G.

Gadaskin, D. D., and A. E. Makovetzki, ii, 101.
Gardiner, J. A., ii, 95.
Garfunkel, A. See A. Rosenheim.
Gautrelot, E., ii, 140.
Gauvry, E., ii, 158.
Geiger, H., and E. Marsden, ii, 92.
Geis, T. See E. Mohr.
Gigon, A. See W. Frey.
Girard, J. See Volcy-Boucher.
Girdwood, G. P., ii, 117.
Gisiger, E. See F. Fichter.
Glaser, E., ii, 101.
Godchot, M., i, 104.
Göttler, M. See A. Einhorn.
Gorboff, A., ii, 111.
Gortner, R. A., *TRANS.*, 110.
Goutal, E., ii, 129, 157.
Grafe, V., i, 148.
Graham, R. P. D., ii, 136.
Gramont, A. de, ii, 85.
Gray, R. W., and Sir W. Ramsay, *TRANS.*, 185.
Graziani, F. See M. Padoa.
Greer, J. R., and F. C. Becht, ii, 141.

Grimbert, L., and E. Bernier, ii, 163.
 Grishkewitsch-Trochimowsky, E.,
 i, 108.
 Grumbach, A., ii, 93.
 Gudzent, F., ii, 140, 146.
 Guertler, W., ii, 128.
 Guglielmo, G., ii, 107.
 Gutbier, A., and M. Riess, i, 97.
 Guye, P. A., and N. Zachariades,
 ii, 116.

H.

Haas, P. See H. R. Le Sueur.
 Haber, F., and B. S. Lacy, ii, 122.
 Hambricht, W. See C. Willgerodt.
 Hanriot, M., i, 95.
 Harding, V. J., and C. Weizmann,
 TRANS., 299.
 Hata, S., ii, 168.
 Hébert, and G. Truffaut, ii, 150.
 Hemsalech, G. A., and C. de Watte-
 ville, ii, 86.
 Henderson, L. J., ii, 139.
 Henderson, Y., ii, 137.
 Henriques, V., and S. P. L. Sören-
 sen, ii, 164.
 Hertel, C. A., ii, 147.
 Hertz, A. F., F. Cook, and E. G.
 Schesinger, ii, 145.
 Herzog, J., and D. Krohn, i, 124.
 Heusler, F., and F. Richarz, ii, 99.
 Heydweiller, A., ii, 106.
 Hicks, W. M., ii, 86.
 Hilditch, T. P. See S. R. Edmin-
 son.
 Hilpert, S., ii, 130.
 Hocheder, F. See R. Willstätter.
 Höckendorf, P., ii, 146.
 Hofmann, K. A., and H. Kirm-
 reuther, with H. Lecher, i, 105.
 Homer, Miss A., and J. E. Purvis,
 TRANS., 280.
 Houben, J., and R. Freund, i, 110.
 Hubert, ii, 152.
 Hug, E. See R. Willstätter.
 Huguot, ii, 155.
 Humfrey, J. C. W. See W. Rosen-
 hain.
 Humphries, H. B. P. See A.
 McKenzie.

J.

Jackson, C. L., and H. A. Flint,
 i, 121.
 Johns, C. O. See H. L. Wheeler.
 Jolibois, P., ii, 132.
 Jolles, A., ii, 164.
 Jones, H. C., and W. W. Strong,
 ii, 87.

Jonker, W. P. A., ii, 127.
 Jorissen, W. P., and N. H. S. van
 Reesema, ii, 122.
 Judd, Miss H. M. See M. O. Forster.
 Just, G., P. Askensasy, and B.
 Mitrofanoff, ii, 96.

K.

Kaluza, L., i, 130.
 Kappeler, H. See F. Fichter.
 Karczag, L. See G. Buglia.
 Kawashima, K., ii, 140.
 Kessler, S. See H. Rupe.
 Khouri, J., ii, 151.
 Kiefer, A. See F. Fichter.
 Kipping, F. S. See F. Challenger.
 Kirmreuther, H. See K. A. Hof-
 mann.
 Kleeman, R. D., ii, 92.
 Koch, W., ii, 142.
 Köhler, F. See E. Mohr.
 Kohlschütter, V., ii, 96.
 Kohn, F. See A. Rosenheim.
 Kohn, M., and F. Bum, i, 136.
 Kolowrat, L., ii, 91.
 Konstaninoff, N. C., ii, 130.
 Kossonogoff, J. J., ii, 97.
 Kostytscheff, S., ii, 148.
 Kowalewsky, K., ii, 147.
 Kramer, E. See A. P. N. Franchi-
 mont.
 Krassa, P., ii, 129.
 Kreglinger. See O. Cohnheim.
 Kreglinger. See O. Cohnheim.
 Kretzer, A., ii, 87.
 Krohn, D. See J. Herzog.
 Kühncl, T. See F. Fichter.
 Kuhn, O., ii, 131.
 Kurbatoff, W. A., and G. G. Eliséeff,
 ii, 102.
 Kurbatoff, W. A. See also G. G.
 Eliséeff.
 Kuzmin, W., i, 109.

L.

Labhardt, H. P. See F. Fichter.
 Lacy, B. S. See F. Haber.
 Lambris, G., ii, 131.
 Landtwing, A. See A. Bistrzycki.
 Le Blanc, M., and L. Bergmann,
 ii, 123.
 Lecher, H. See K. A. Hofmann.
 Lehmann, F. See E. Rupp.
 Lehmann, R. See L. Weiss.
 Lepape, A. See C. Mourou.
 Le Pla, M. See J. F. Spencer.
 Leprince, M. See E. Perrot.
 Le Sueur, H. R., and P. Haas,
 TRANS., 173.

Leyko, Z., and L. Marchlewski, i, 144.
 Limpach, O. See M. Busch.
 Lissner, A., ii, 156.
 Loquin, R. See L. Bouveault.
 Loeb, J., ii, 147.
 Loh, W., and G. Pulvermacher, i, 94, 95.
 Löwy, E., i, 123.
 Löwy, M., ii, 168.
 Luniak, A., i, 90.
 Luniak, A. See also E. Fischer.
 Lutz, G. See F. Straus.
 Lutz, O., and R. Svinno, ii, 156.

M.

McFarland, D. F. See H. L. Wheeler.
 McKenzie, A., and H. B. P. Humphries, TRANS., 121.
 MacLean, H., ii, 142.
 MacLean, H., and O. T. Williams, ii, 142.
 Macleod, J. J. R., and R. G. Pearce, ii, 144.
 Maillard, L. C., i, 138.
 Makovetzki, A. E., ii, 101.
 Makovetzki, A. E. See also D. D. Gadaskin.
 Makower, W., and S. Russ, ii, 91.
 Malaquin, P., ii, 165.
 Malvezin, P., i, 91; ii, 151.
 Manchot, W., and W. Brandt, i, 85; ii, 137.
 Mandel, J. A., i, 147.
 Marchlewski, L. See Z. Leyko.
 Marino, L., ii, 126, 155.
 Margailan, L., ii, 163.
 Marsden, E. See H. Geiger.
 Matzurevitch, I., i, 89.
 Mauthner, F., i, 115.
 Mayer, F. See M. Freund.
 Mendel, L. B. See H. L. Wheeler.
 Meslin, G., ii, 99.
 Meyer, A. See A. Wahl.
 Michaelis, L., and P. Rona, ii, 139, 163.
 Migay, T. J., and W. W. Sawitsch, ii, 140.
 Milobendski, T., ii, 154.
 Mitrofanoff, B. See G. Just.
 Miller, O., and J. Smirnof, i, 121.
 Mohr, E., and T. Geis, i, 117.
 Mohr, E., and F. Köhler, i, 116.
 Moore, C. W. See F. B. Power.
 Moureu, C., and A. Lepape, ii, 136.
 Müller, R. See M. O. Forster.
 Muller, J. A., ii, 154, 159.
 Muller, P. T., ii, 118.

N.

Němeček, H. See E. Votoček.
 Nerking, J., ii, 162.
 Nierenstein, M., and T. A. Webster, i, 124.

O.

Obladen, H. See F. Fichter.
 Oesterle, O. A., and G. Riat, i, 128.
 Olie, jun., J. See E. Cohen.

P.

Padoa, M., and F. Graziani, i, 135.
 Pantanelli, E., and M. Sella, ii, 149.
 Pascal, P., ii, 100.
 Patterson, T. S., ii, 107.
 Pearce, R. G. See J. J. R. Macleod.
 Pélabon, H., ii, 119.
 Perkin, A. G., TRANS., 220.
 Perkin, W. H., jun., and R. Robinson, TRANS., 305.
 Perrot, E., and M. Leprince, ii, 151.
 Peters, W., ii, 114.
 Piloty, O., and E. Quitmann, i, 133.
 Plancher, G., and U. Ponti, i, 132.
 Pochettino, A., ii, 89, 119.
 Pohl, R., ii, 90.
 Ponti, U. See G. Plancher.
 Porcher, C., ii, 144.
 Power, F. B., and C. W. Moore, TRANS., 99.
 Power, F. B., and A. H. Salway, TRANS., 231.
 Pozzi-Escot, M. E., ii, 148, 153, 155, 160.
 Prandtl, W., and B. Bleyer, ii, 134.
 Preuner, G., and W. Schupp, ii, 118.
 Prileschaeff, N., i, 86.
 Prochnow, A., ii, 163.
 Przyłuska, M., i, 106.
 Pulvermacher, G. See W. Löb.
 Purvis, J. E. See Miss A. Homer.
 Pyman, F. L., TRANS., 264.

Q.

Quitmann, E. See O. Piloty.

R.

Ramsay, Sir W. See R. W. Gray.
 Rassenfossé, A., ii, 89.
 Rechenberg, C. von, ii, 101.
 Reddellien, G., i, 118.

Reeseema, N. H. S. van. See W. P. Jorissen.
 Reichard, C. J., ii, 163.
 Reinhard, A. See W. Zaleski.
 Reinhardt, J. See M. Busch.
 Keythler, A., ii, 104.
 Riat, G. See O. A. Oesterle.
 Richarz, F. See F. Heusler.
 Riegel, E. R. See C. R. Sanger.
 Riesenfeld, E. H., ii, 126.
 Riess, M. See A. Gutbier.
 Roberts, E. J. See P. E. Browning.
 Robinson, J., ii, 93.
 Robinson, R. See W. H. Perkin, jun.
 Rodenburg, J. See G. C. A. van Dorp.
 Rohland, P., ii, 104, 125, 129.
 Rona, P. See L. Michaelis.
 Roschdestvensky, M. S., i, 107.
 Roschdestvensky, M. S. See also A. G. Doroschewsky.
 Rosenhain, W., and J. C. W. Humfrey, ii, 128.
 Rosenheim, A., A. Garfunkel, and F. Kohn, i, 101.
 Rosemund, K. W., i, 106.
 Royds, T., ii, 87.
 Rupe, H., and S. Kessler, i, 93.
 Rupp, E., and F. Lehmann, ii, 163.
 Russ, S. See W. Makower.

S.

Sacher, J. F., ii, 158.
 Sackur, O., ii, 113.
 Saiki, T., ii, 117, 142, 146.
 Saiki, T. See also S. R. Benedict.
 Salkowski, E., ii, 142.
 Salway, A. H. See F. B. Power.
 Sanchez, J. A., ii, 153.
 Sanger, C. R., and E. R. Riegel, ii, 161.
 Sasaki, T., ii, 166.
 Sato, T., ii, 166.
 Sawitsch, W. W. See T. J. Migay.
 Scala, A., and G. Bonamartini, i, 146.
 Scalinci, N. See F. Bottazzi.
 Scharff, E. See T. Zincke.
 Schenck, M., i, 99, 100.
 Schiff, R., i, 134.
 Schlesinger, E. G. See A. F. Hertz.
 Scholtz, M., i, 96.
 Schroeder, J. von, i, 129.
 Schumm, O., ii, 167.
 Schupp, W. See G. Preuner.
 Sella, M. See E. Paptanelli.
 Sewerin, S. A., ii, 148.
 Sidersky, D., ii, 161.

Stieber, N., ii, 147.
 Smiles, S. See E. de B. Barnett.
 Smirnoff, J. See O. Miller.
 Smirnoff, W. A., i, 104.
 Sörensen, S. P. L., i, 147.
 Sörensen, S. P. L. See also V. Henriques.
 Sonnenburg, E. F. See H. T. Bucherer.
 Spencer, J. F., and M. Le Pla, ii, 97.
 Spring, W., ii, 126.
 Staudinger, H., and S. Bereza, i, 89.
 Stock, A., ii, 121.
 Stoecklin, E. de, ii, 162.
 Stoermer, K., i, 114.
 Stoll, A. See R. Willstätter.
 Storey, W. F. See H. L. Wheeler.
 Straus, F., with A. Ackermann and G. Lutz, i, 119.
 Strong, W. W. See H. C. Jones.
 Sutherland, W., ii, 116.
 Svedberg, T., ii, 103.
 Svinne, R. See O. Lutz.
 Swietoslowski, W., ii, 102.

T.

Tananaeff, N., and D. Tsukerman, ii, 158.
 Tarasoff, B., i, 109.
 Taylor, J. M., ii, 158.
 Terroine, E. F., ii, 141.
 Testoni, G., ii, 167.
 Thar, H., ii, 141.
 Thoms, H., i, 122.
 Thorpe, Sir T. E., TRANS., 161.
 Titherley, A. W., TRANS., 200.
 Tóth, J., ii, 165.
 Trautz, M., ii, 114.
 Trivelli, A. P. H., ii, 90.
 Tröger, J., and H. Bremer, i, 113.
 Truffaut, G. See A. Hébert.
 Truffi, M., ii, 142.
 Tschernik, G. P., ii, 136.
 Tsukerman, D. See N. Tananaeff.
 Tutton, A. E. H., ii, 127.
 Twiss, D. F. See P. F. Frankland.

U.

Ultée, A. J., i, 132.
 Urban, J. See K. Andrlík.
 Ury, H., ii, 145.

V.

Vandavelde, A. J. J., ii, 141.
 Vernadsky, W. L., ii, 136.

Vigouroux, E., ii, 132.
Voisenet, E., i, 91.
Volcy-Bouchet, and J. Girard,
ii, 162.
Voto ek, E., and H. Němeček, i, 95.

W.

Waentig, P., ii, 117.
Wahl, A., and A. Meyer, i, 134.
Wartenberg, H. von, ii, 134.
Watteville, C. de. See G. A.
Hemsalech.
Webster, T. A. See M. Nierenstein.
Weiss, L., and T. Engelhardt,
ii, 122.
Weiss, L., and R. Lehmann, ii, 133.
Weizmann, C. See V. J. Harding.
Welsbach, C. A. von, ii, 128.
Wheeler, H. L., and C. O. Johns,
i, 114.
Wheeler, H. L., and D. F. McFar-
land with W. F. Storey, i, 133.
Wheeler, H. L., and L. B. Mendel,
ii, 143.
Willgerodt, C., and W. Hambrecht,
i, 117.

Williams, O. T. See H. MacLean.
Willstätter, R., and H. Fritzsche,
i, 128.
Willstätter, R., F. Hocheder, and
E. Hug, ii, 150.
Willstätter, R., and A. Stoll, i, 134.
Winther, C., ii, 115.
Wolter, L., ii, 160.
Wren, Miss G. H. See A. W. Cross-
ley.
Wroczyński, A. See E. Briner.

Y.

Yoshida, T., ii, 164.

Z.

Zachariades, N. See P. A. Guye.
Zaleski, W., ii, 149.
Zaleski, W., and A. Reinhard,
ii, 143.
Zeisel, S., and M. Daniek, i, 92.
Zemplén, G. See E. Fischer.
Zerewitinoff, T., i, 143.
Ziffer, F. See A. Eisenstein.
Zinke, T., and E. Scharff, i, 140.

JOURNAL
OF
THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

Photometric Measurements with the Coloured Bunsen Flame. ERNST BECKMANN and PERCY WAENTIG (*Zeitsch. physika Chem.*, 1909, **68**, 385—439).—A new arrangement for supplying salt to a flame, which gives constant and readily reproducible results is described and figured. A salt solution is allowed to drop on a disk kept in rapid rotation, and the fine-spray thus produced is carried away by the stream of gas, drops of liquid being retained. The different factors determining the properties of the flame, more particularly the velocity of rotation of the disk, the rate of supply of the salt solution and of the gas, can be varied independently, and the effect of each is described in detail. The method of determining the amount of salt supplied to the flame depends on the property of the silent electric discharge in condensing dust particles; for this purpose the gas charged with salt particles is passed through Siemens' ozone tube, and the salt deposited after a considerable interval removed and weighed.

The effect of anions on the intensity of the flame was determined by measurements with a König-Martens-Grünbaum photometer. For the alkali metals, the salts of oxygen acids give a rather more intense flame than the halogen salts, but hydrogen peroxide does not appreciably increase the intensity. As regards the alkaline earth metals, the intensity for the halogen salts of calcium is greater than for

the salts of oxygen acids, but barium salts show the converse behaviour. In the case of strontium and lithium salts, change of the anion alters even the tint of the flame.

Foreign salts, including both those which colour and do not colour the flame, diminish the intensity of the colour, and both anion and cation seem to take part in this effect. The diminution increases with increasing proportion of the salt added, and the effect appears to be the greater the higher the equivalent weight of the cation.

Accurate measurements have been made on the relationship between the concentration of the salt solution and the amount of salt conveyed into the flame. For the solution of a single salt, the ratio between the salt sprayed and the concentration of the salt solution is constant, but for mixtures of salts, especially in concentrated solution, the amount converted into spray is relatively smaller. According to Arrhenius (Abstr., 1891, 5, 515) and Gouy (*Ann. Chim. Phys.*, 1879, [v], 18, 5), the intensity of the colour in the flame and the electrical conductivity are proportional to the square root of the concentration of the salt in the flame. The authors find, however, that these laws hold only for certain salts under certain definite conditions. On the other hand, the effect of the anions on the intensity is parallel to that on the electrical conductivity, and there is doubtless a close connexion between luminosity and electrical conductivity.

G. S.

Spectral Analytical Investigation of the Glow Light at Points. HERMANN VON DECHEND (*Ann. Physik*, 1903, [iv], 30, 719—745).—The spectra of the glow which accompanies electric discharge between points have been investigated. The discharge was allowed to take place between platinum and aluminium electrodes in tubes containing different gases.

In the case of oxygen, nitrogen, and chlorine, the point discharge spectrum is similar to that obtained by the use of Geissler tubes. With nitrogen, nitric oxide, and air, which all show the first banded spectrum of nitrogen, the light emission is not confined to the immediate neighbourhood of the points, but is spread out through the space between the electrodes. Hydrogen also exhibits a second luminous region, and this takes the form of a luminous stream of negatively charged ions, which are emitted from the cathode in a direction which is independent of the position of the anode. The spectrum of this luminous stream consists of indistinct lines which do not coincide with the lines of any known spectrum. On the other hand, the spectrum of the glow at the points consists of the first and second hydrogen spectra.

Observations were also made with hydrogen chloride, methane, carbon monoxide, and carbon dioxide. All these gases are decomposed by the point discharge. Hydrogen chloride shows the stronger chlorine lines, some of the hydrogen lines, and also a continuous spectrum. Methane exhibits hydrogen lines and the Swan spectrum. Carbon monoxide and carbon dioxide, which give the same Geissler tube spectrum, behave differently in the case of point discharge. The former shows all the chief bands of the carbon monoxide spectrum, while the latter only gives the band at 4123.

H. M. D.

Band Spectra of Barium and Aluminium. P. E. LECOQ DE BOISBAUDRAN (*Compt. rend.*, 1909, 149, 899—903. Compare *Trans.*, 1909, 95, 279).—The author believes that the bands in the spectra of salts of barium and aluminium are due to the metals (compare Börsch, *Abstr.*, 1909, ii, 775), and that they result from disturbances of the simpler vibrations which are predominant at high temperatures. Certain relations which hold between the frequencies of the right, that is, the most refrangible, edges of the bands of barium and aluminium are also developed.

T. S. P.

Systems of Series in the Spectra of Zinc, Cadmium, and Mercury. FRIEDRICH PASCHEN (*Ann. Physik*, 1909, [iv], 30, 746—754).—An examination of the data of various observers shows that the spectra of zinc, cadmium, and mercury contain three series of lines which are analogous to those found in the spectrum of magnesium.

H. M. D.

Influence of Dilution on the Colour and the Absorption Spectra of Various Permanganates. JOHN E. PURVIS (*Proc. Camb. Phil. Soc.*, 1909, 15, 247—256).—The author has compared the photographs of the absorption spectra of aqueous solutions of barium, zinc, and potassium permanganate containing 0.001 gram-molecule per litre and of solutions prepared from these by diluting 30.8 and 62 times respectively. The freshly prepared solutions exhibit differences in the width of the bands and also in the amount of general absorption, at the more refrangible end of the spectrum. On keeping, the two series of diluted solutions exhibit changes in colour which are accompanied by changes in the width of the bands and an increase in the general absorption. In the case of the most dilute series, the brownish-yellow colour which is developed is attended by an almost complete obliteration of the absorption bands. The observed changes take place whether the solutions are insulated or kept in the dark, but the rate of change is increased by light. The changes in colour are supposed to be due to a decomposition of the permanganate ions under the influence of the solvent.

H. M. D.

Relations between Constitution and Absorption towards the Violet End of the Spectrum for Solutions of certain Chromium and Iron Salts. ALFRED BYK and H. JAFFE (*Zeitsch. physikal. Chem.*, 1909, 68, 323—356).—The observations were made with an instrument provided with quartz lenses and prisms, and the spectra were photographed. The limits of absorption for the different solutions are given in tabular form. Most of the chromium salts were used in dilutions from $\frac{1}{2}$ to $\frac{1}{10}$ molar, but the iron salts were used also in much greater dilution.

All the solutions of violet chromium salts show similar absorption band 461μ to 364.5μ ; beginning of complete absorption about 260μ in $\frac{1}{2}$ molar solution, which is therefore due to the chromium ion. The band becomes narrower with increasing dilution. Slight deviations with the nitrate are doubtless due to the absorption of the NO_3 ion.

In solutions of green, complex chromium salts the absorption band and the limit of complete absorption are both shifted towards the red end of the spectrum. Each solution has, however, its own individual spectrum, and the more completely the electrons are displaced by radicals the greater is the displacement towards the red end. For the influence of acids (added to the green solutions) on the spectra, which is somewhat complicated, the original paper must be consulted.

Neutral concentrated solutions of ferric alum and of ferric nitrate are reddish-brown, the corresponding solutions of ferric chloride are yellowish-brown, and there are corresponding differences in the absorption spectra. Hydrochloric acid darkens the colour of ferric chloride solutions, probably owing to the formation of the complex FeCl_3 , which has greater absorbing power than the ion Fe^{+++} . The addition of sulphuric acid lightens the colour of iron alum, a result probably connected with diminution of hydrolysis. In very dilute solutions, on the other hand, the addition of sulphuric acid increases the absorption, probably owing to the change of Fe^{+++} ions to complex ions. Ferric chloride has greater absorption than the fluoride, corresponding with the greater weight of the chlorine atoms.

With increasing dilution, ferrous salts show more distinctly the absorption characteristic of Fe^{++} ions.

For all the salts examined, non-ionised chlorides have greater absorbing power than the corresponding sulphates. G. S.

Relationship between the Colour and Constitution of Unsaturated Ketones and their Salts. HANS STOBBE, RICHARD HAERTEL, and SIEGFRIED SEYDEL (*Annalen*, 1909, 370, 93—99, 99—129, 129—141).—See this vol., i, 43, 45.

Polychroism of Artificially Coloured Crystals. PAUL GAUBERT (*Compt. rend.*, 1909, 149, 1004—1006).—The author has previously shown that artificially coloured crystals may be polychoic, and that they may be divided into two classes. In the first class the colouring matter is in a state of solution in the crystals, whilst in the second class it exists in the form of crystals, the orientation of which may be different from that of the crystal occluding them. Lehmann has put forward the idea that there is a relation between the intensity of the polychroism and the double refraction of a coloured crystal. The author shows that this only holds for crystals belonging to the first class. In crystals of phthalic acid, meconic acid, carbamido nitrate, carbamide oxalate, phloridzin, and chrysotile, coloured by methylene-blue, which belong to the first class, the differences between the amounts of light absorption in the two optical axes increase with the amount of double refraction.

Crystals, such as lead nitrate and barium nitrate, when coloured with methylene-blue belong to the second class. They show an intense polychroism, although they are only very feebly doubly refracting.

The connexion between polychroism and double refraction, as indicated above, may be used to classify other coloured crystals.

T. S. P.

Luminescence Phenomena in Certain Organic Compounds. ALFREDO POCHETTINO (*Atti R. Accad. Lincei*, 1909, [v], 13, ii, 358—365).—It is stated in the text-books that no phosphorescent liquid is known, with the possible exception of liquid oxygen. But the author has shown previously (*ibid.*, 1905, [v], 14, ii, 222) that the mineral oil usually employed in Geryk pumps (which in ordinary light exhibits a marked greenish-yellow fluorescence) gives under the influence of cathode rays a vivid dark blue luminescence, which disappears sensibly at the same time as the excitation ceases; similar luminescence is obtained with the oil after solidification at the temperature of liquid air, but in this case it persists five to ten seconds after the cessation of the cathode rays. The influence of the state of aggregation on the luminescence is also shown by ordinary wax, which, when solid, exhibits a pale yellowish-sky-blue, and, when liquid, a dark blue, cathodic luminescence.

The luminescence effects of anthracene, phenanthrene, fluorene, and retene were studied in four tubes: (1) a cathode ray tube, (2) an anode ray tube, (3) a horizontal tube with symmetrical plane electrodes, and (4) a tube in which the distance between substance and cathode can be varied, the change of state being effected by the thermal action of the cathode rays themselves.

Also in tube (1) the following substances, all capable of exhibiting ordinary fluorescence in suitable solutions, were examined: alizarin, phthalic anhydride, anthranilic acid, rhodamine, α - and β -naphthylamines, α - and β -naphthols, phthalimide, euphosphine, aminonaphtholdisulphonic acid, β -naphthol- β -sulphonic acid, vaselin, and naphthalene.

The luminescence emitted by the monoclinic laminae of anthracene or phenanthrene, or by the trimetric prisms of phthalic anhydride or α -naphthylamine, shows no appreciable polarisation. The behaviour of the above substances in the vacuum tubes indicates that with most of them the state of aggregation exerts a marked influence on the colour of the cathodic luminescence, the colour changing at the moment of fusion and changing again to the original one on re-solidification. Then, too, certain of the substances are luminescent only when either liquid or solid. The changes of colour as the degree of evacuation is increased are also discussed.

T. H. P.

Phosphorescence of some Inorganic Salts. JOHN ANDERSON WILKINSON (*J. Physical Chem.*, 1909, 13, 691—728).—Experiments are described which show the existence of a relationship between phosphorescence and chemical action. When aqueous solutions of chlorides, bromides, iodides, and sulphates are electrolysed with anodes of copper, mercury, silver, cadmium, zinc, potassium, and sodium, the salt formation at the anode is in many cases accompanied by the emission of light, the colour of which in most cases resembles that of the fluorescent and phosphorescent light emitted under the influence of cathode rays.

Similar luminous effects are also obtained when the metals enter into direct combination with the halogens or oxygen at elevated

temperatures. In the case of sodium and potassium, the colour of the light emitted varies with the rate of combination. The colour of the phosphorescent light corresponds with that emitted when slow combination takes place.

Certain salts, said to be phosphorescent, were found not to be so when pure, but phosphorescence could be induced by the addition of small quantities of other salts. Sodium peroxide shows fluorescence and phosphorescence under the action of cathode rays if a good vacuum is maintained. The fluorescence of aluminium oxide under the same conditions is traced to the presence of sodium in the form of peroxide or the aluminate. H. M. D.

Electrical Behaviour of Fluorescing Iodine Vapour. R. WHIDDINGTON (*Proc. Camb. Phil. Soc.*, 1909, 15, 189).—A beam from an arc light was focussed on iodine vapour between two copper electrodes. Although fluorescence was plainly visible, no trace of ionisation could be detected even when the applied electric field was almost sufficient to produce discharge. The experiment shows that fluorescence is not necessarily accompanied by ionisation. H. M. D.

Optical Activity of the Asymmetric Atom. A. E. EVEREST (*Chem. News*, 1909, 100, 295).—Perkin, Pope, and Wallach have recently resolved 1-methyl- Δ^3 -cyclohexylidene-4-acetic acid into two enantiomorphous forms, and claim that in this case optical activity is due to enantiomorphous, molecular configuration and not to the presence of an asymmetric atom (*Trans.*, 1909, 95, 1789). The author contends that the carbon atom numbered 1 in the formula given in the original paper (*loc. cit.*, 1792) is asymmetric by reason of its position in relation to the H- and CO_2H groups marked *c* and *d* respectively in the same formula. *p*-Methylcyclohexylcarboxylic acid at first sight appears to contain two asymmetric carbon atoms, as here defined, but this apparent analogy disappears when it is remembered that the H- and CO_2H - groups (and also the H- and CH_3 - groups occupying similar positions in relation to the carbon atom marked 4) in the original formula (*loc. cit.*) in this case are in a plane at right angles to the ring. T. A. H.

Attempts at Asymmetric Synthesis by means of Circularly polarised Light. MAURICE PADOA (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 390—392).—The action of bromine on a carbon disulphide solution of angelic acid under the influence of circularly polarised light yields only optically inactive products (compare Wislicenus, *Abstr.*, 1893, i, 135, 455; Cotton, *Abstr.*, 1909, ii, 278). T. H. P.

Photochemical Action. II. EMIL WARBURG (*Ber. Deut. physikal. Ges.*, 1909, 654—660. Compare *ibid.*, 1907, 753).—The transformability of radiant energy is considered with reference to a gas which is photochemically sensitive, and in which the photochemical change can also be brought about by a change of temperature. If T_1 and T_2 denote respectively the temperature of the gas and that

corresponding with the incident radiation, T_s the temperature corresponding with the shift of the equilibrium between the gas and its products of dissociation consequent on the absorption of the radiant energy, Q_s the amount of energy absorbed, and q the heat of formation of the gas from its dissociation products, then it is shown that $q/T_s - Q_s/T_s + (Q_s - q)/T_s \geq 0$. If the whole of the absorbed energy is used up in the chemical transformation, then $Q_s = q$ and $T_s \leq T_s$. According to this relationship, the chemical decomposition of the photochemically sensitive gas reaches a limit when the change in the concentration of the products of dissociation has reached a point which corresponds with the temperature of the incident radiation. The application of the deduced relationship to the dissociation of carbon dioxide and the conversion of oxygen into ozone is considered.

H. M. D.

Apparatus for Measuring Radioactivity. BÉLA SZILÁRD (*Compt. rend.*, 1909, 149, 912—914).—The gold leaf of the electroscope is replaced by a steel needle, mounted horizontally. The needle is magnetised, and in the zero position it lies in the magnetic meridian. When in this position it is encased by a metallic ribbon, with which it is connected electrically. The whole is mounted in a box fitted with a plate and ring of soft iron, in order to screen the needle from external influences. The deviation of the needle is a measure of the charge given to the system when, for example, a radioactive substance is introduced into the box. The whole apparatus is portable.

T. S. P.

The Scattering of the β -Rays of Radium. JOHN P. V. MADSEN (*Phil. Mag.*, 1909, [vi], 18, 909—915. Compare Crowther, *Abstr.*, 1908, ii, 247).—These results confirm the experiments of Crowther with the β -rays of uranium. The scattering of the β -rays of radium by thin films of material has been found to be unsymmetrical about a plane at right angles to the direction of the radiation, more emerging in the original direction than are returned. Gold turns back a greater proportion of the scattered radiation than aluminium. The emergent scattered radiation attains a maximum with 0.013 cm. aluminium and 0.0008 cm. gold. There is thus a close parallel between the scattering of β - and γ -rays (Madsen, *Abstr.*, 1909, ii, 365), which is in support of Bragg's discrete or neutral-pair theory of the γ -rays. The results of McClelland on secondary β -rays (*Abstr.*, 1908, ii, 651) are regarded as explicable without the need of supposing that there exists a true secondary radiation proceeding from the atoms affected by incident β -rays.

F. S.

Passage of β -Rays through Matter. HEINRICH W. SCHMIDT (*Physikal. Zeitsch.*, 1909, 10, 929—948).—Experiments have been made to determine whether the absorption of β -rays takes place exactly according to an exponential law. In order that this may be the case, it is necessary that the penetrating power of homogeneous β -rays should be constant and independent of the thickness of matter traversed.

Measurements were made on the β -rays emitted by radium-E and by uranium-X. These were allowed to fall on metal plates, and the penetrating power of the incidence and emergence radiation was compared.

From the experimental results, the conclusion is drawn that β -rays experience a slight diminution in velocity in their passage through matter. The magnitude of this diminution increases as the atomic weight of the traversed substance decreases. It also increases with the extent to which the β -rays are diverted from their original direction of movement. In accordance with this, it is found that for thin layers of material, the amount of transmitted β -radiation diminishes more quickly than corresponds with an exponential law. This is equivalent to a diminution in the penetrating power as the thickness of the absorbing material increases.

In addition to various metals, the absorption of the β -rays in gases was also examined. In comparison with air, hydrogen is found to be very highly ionised by the β -rays. This is in agreement with the general result that elements of low atomic weight have a relatively large absorption capacity.

H. M. D.

Law of Absorption of the β -Rays. OTTO HAHN and LISE MEITNER (*Physikal. Zeitsch.*, 1909, 10, 948—950).—The conclusions drawn by Wilson (*Proc. Roy. Soc.*, 1909, A, 82, 612) from an investigation of the absorption of homogeneous β -rays are opposed to the results obtained by the authors in similar measurements. A critical examination of the experimental arrangement adopted by Wilson shows that the rays examined were not homogeneous, and that his conclusions are therefore untenable.

H. M. D.

Phenomena of X-Ray Transmission. CHARLES G. BARKER (*Proc. Camb. Phil. Soc.*, 1909, 15, 257—268).—The relationships between the various phenomena which accompany the transmission of Röntgen rays are discussed. It is shown that there is an intimate connexion between the absorption of the primary radiation in a substance, the ionisation in the absorbing substance (when in the gaseous state), and the intensity of the secondary radiation from the absorbing substance. These are periodic functions of the penetrating power of the primary radiation, the three rising and falling together. The periodicity in intensity of the secondary radiation is not one of intensity alone, for each fresh period brings a characteristic radiation of different penetrating power.

H. M. D.

Alteration in the Colour of the Diamond under the Action of Various Physical Agents. PAUL SACERDOTE (*Compt. rend.*, 1909, 149, 993—994. Compare Abstr., 1906, ii, 863; 1907, ii, 956).—Diamonds varying in colour from colourless to a greenish-yellow have been submitted successively to the action of X-rays, cathode rays, and a temperature of 300—400°. The duration of the experiments varied from some minutes to a few days.

X-rays have no sensible effect on the colour. Cathode rays gradually deepen the initial colour (colourless diamonds become coloured).

through a wine-red to a more or less deep brown, depending on the time of action. The colours so obtained seem to be stable, since diamonds so coloured have been kept for a year or so.

Exposure to a temperature of 300—400° rapidly converts the diamond to its original colour.

T. S. P.

Influence of Radium X-Rays and Cathode Rays on Various Precious Stones. ANDRÉ MEYÈRE (*Compt. rend.*, 1909, 149, 994—995).—Diamonds and different varieties of corundum (sapphire, white sapphire, ruby) have been submitted to the action of X-rays, cathode rays, and of radium. In some cases the stones were placed outside the X-ray tube; in other cases they were submitted to the action of X-rays and cathode rays by being placed inside the tube. For the electrodes of the tubes, different combinations of copper, nickel, aluminium, and platinum were used, and in all experiments the vacuum in the tube was maintained by the continuous working of a mercury pump. In some experiments the current was only passed at intervals of some seconds, in order to avoid heating the stones.

In all cases the corundums and diamond become more or less brown in colour (compare preceding abstract).

T. S. P.

Influence of Radium Rays on the Coloration of Sanidin, Zircon, and Quartz. Crystalline Form of the Zircon in Sanidinite from the Laacher See. R. BRAUNS (*Centr. Min.*, 1909, 23, 721—728).—Observations are recorded which show that certain naturally colourless forms of zircon are coloured when subjected to the action of radium. A similar effect is also found in the case of certain coloured varieties of zircon and quartz which have been decolorised by heating. On the other hand, colourless zircon from Pfitsch and colourless quartz are unacted on by radium. The colour effects are attributed to the presence in the minerals of foreign substances which are acted on by radium rays. Crystallographic measurements of two forms of zircon occurring in the sanidinite of the Laacher See are recorded.

H. M. D.

Accumulation of Helium in Geological Time. II. ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1909, A, 83, 98—99. Compare Abstr., 1908, ii, 922).—The amount of helium in ironstones from various localities has been determined. The results are given in terms of the "helium ratio," which expresses the amount of helium in c.c. per gram of total equivalent uranium oxide. It is found that one gram of thorium is equivalent to 0.203 gram of uranium oxide so far as the production of helium is concerned, and the expression "total equivalent uranium oxide" represents therefore the quantity of uranium oxide plus 0.203 time the quantity of thorium in a mineral. The helium ratio thus defined is found to vary from 0.76 to 13.3.

With regard to the rate of formation of helium from the uranium and thorium series of substances, direct measurements have given 10.4×10^{-8} c.c. per gram of uranium oxide per annum. This is in good agreement with Rutherford's indirectly obtained value of

9.13×10^{-8} c.c. No accurate value has yet been obtained for the thorium series, but the rate is certainly smaller than in the case of uranium.

H. M. D.

The Relation between Uranium and Radium. IV. FREDERICK SODDY (*Phil. Mag.*, 1909, [vi], 18, 846—858. Compare Abstr., 1908, ii, 919).—The three uranium solutions purified by Mackenzie in 1905–1906 have all shown during the past year an increase in the quantity of radium present. The methods of measuring the radium have been improved in detail, and are now accurate to about 10^{-13} gram. The rate of growth of radium in all three solutions has been proportional to the square of the time since purification. In the oldest solution, containing 250 grams of uranium, the radium in the last year has increased from 19.6 to 24.3 ($\times 10^{-12}$ grams). The period of average life of the intermediate substance (ionium) is calculated to be 18,500 years, assuming there is only one. The existence of a new relatively short-lived intermediate product in the series is indicated, retarding still further the rate of growth of radium initially. Such a substance, if it exists, would reduce the period above referred to, which is therefore a maximum estimate. F. S.

The Rays and Products of Uranium-X. FREDERICK SODDY (*Phil. Mag.*, 1909, [vi], 18, 858—865. Compare Abstr., 1909, ii, 459, 460).—On the view that the direct parent of radium is the direct product of uranium-X, powerful preparations of the latter should develop a feeble α -radiation as the uranium-X disintegrates and its β -radiation decays. From the maximum period of the parent of radium (compare preceding abstract) it is calculated that the uranium-X in equilibrium with 1 kilogram of uranium should give a product having the α -activity of 2 mg. of uranium. This it has been now shown not to do. Measurements of the α -activity of several preparations of uranium-X, prepared from 50 kilos. of uranyl nitrate, in an intense magnetic field in hydrogen to minimise the powerful β -radiation, have shown in all the presence of a constant feeble α -radiation from the start, due apparently to a substance genetically unconnected with uranium-X, but separated with it (possibly ionium). The earlier observations of a rapid growth of α -rays (Abstr., 1909, ii, 460) have not since been confirmed by more perfect methods and are rejected. The conclusion arrived at is that the direct parent of radium cannot be the direct product of uranium-X, and it is doubtful whether it can be a product at all. The difficultly deviable β -radiation of uranium-X appears to resemble ordinary β -rays, but shows an anomalous behaviour in certain respects. F. S.

Experimental Study of the Large Ions in the Air. S. G. LUSBY (*J. Roy. Soc. New South Wales*, 1909, 43, 55—60).—Measurements have been made of the mobility of the slowly-moving ions which are present in the air, and also of the removal of these ions under the influence of drying agents and the rate at which they are reproduced. The apparatus is similar to that described previously by Zeleny. The number of the large ions, as well as of the small

ions, is considerably reduced when the air is passed over calcium chloride or phosphoric oxide before it enters the testing apparatus. The reduction amounts to 50% when the air is dried as completely as possible by passing over a sufficiently long column of phosphoric oxide. If the large ions are completely removed by an electric field, it is found that an interval of about twenty-two minutes elapses before the number of ions in unit volume attains its original value.

H. M. D.

Mobility of the Large Ions in the Air. JAMES A. POLLOCK (*J. Roy. Soc. New South Wales*, 1909, 43, 61—68. Compare preceding abstract).—The mobility of the slowly-moving ions in the air is found to depend on the amount of moisture present. When the amount of moisture is altered to a considerable extent, an interval of several minutes elapses before the ions are in equilibrium with the new vapour-pressure conditions.

H. M. D.

Ionisation in Various Gases. F. PARR METCALFE (*Phil. Mag.*, 1909, [vi], 18, 878—889).—In order to ascertain whether the ionisation produced in different gases can be represented as the sum of the ionisations contributed by the atoms composing the molecules, experiments have been made on gases representing series of compounds containing the same two elements. The α -radiation from thin layers of uranium oxide was used as the ionising agent. The pressure of the different gases in the ionisation chamber was adjusted so that the stopping-power for the α -rays was approximately the same in every case.

For hydrogen, methane, ethane, propane, butane, and pentane, the relationship between the molecular ionisation and chemical composition is such that the addition of CH_2 to the molecule increases the molecular ionisation by an approximately constant amount, 0.92. Deducting 0.23 as the contribution of the two atoms of hydrogen, the value for carbon is found to be 0.69. This is very nearly the same as the value obtained for carbon from the series: methyl, ethyl, and butyl alcohols. On the other hand, the series oxygen, carbon dioxide, carbon monoxide yields for carbon the value 0.42. No simple additive relationship is evident in the series oxygen, nitric oxide, nitrous oxide.

From the results the conclusion is drawn that the contribution of an atom to the molecular ionisation is not constant, although for series of related compounds an additive law appears to be closely followed in some cases.

H. M. D.

Chemical Reactions and the Ionisation of Gases. MAURICE DE BROGLIE and L. BRIZARD (*Compt. rend.*, 1909, 149, 923—924).—Previous experiments of the authors have led them to the conclusion that the ionisation of a gas produced in a chemical reaction, or of a gas in which a reaction takes place, is not due to the chemical reaction itself, but to other causes (compare Abstr., 1909, ii, 637). Reboul (*ibid.*, ii, 718) has found, however, that air containing the fumes of ammonium chloride, formed by the combination of ammonia and hydrogen chloride, is ionised to a considerable extent; also that the

oxidation of a freshly-cut surface of sodium or of aluminium amalgam, or the formation of nitrous fumes, gives rise to conducting gases. The authors have repeated Reboul's experiments, taking great care to eliminate disturbing causes which would give rise to conduction, and find that under these conditions no gaseous ionisation takes place.

T. S. P.

Dielectric Constants of the Halogen Hydrides. OSCAR C. SCHAEFER and HERMAN SCHLUNDT (*J. Physical Chem.*, 1909, 13, 669—672).—The dielectric constants of the liquid halogen hydrides were determined by Drude's method at two different temperatures with the following results: Hydrogen chloride, 4.60 and 8.85 at 27.7° and -90°; hydrogen bromide, 3.82 and 6.29 at 24.7° and -80°; hydrogen iodide, 2.90 and 2.88 at 21.7° and -50°. Solid hydrogen iodide gave 3.95 at -70°, and solid hydrogen cyanide, 2.4 and 3.05 at -25° and -70° respectively.

The low values of the dielectric constant are anomalous in view of the fact that the liquid halogen hydrides yield solutions of high conducting power when certain organic acids and alcohols are dissolved in them. The conclusion seems inevitable that other factors besides the dielectric constant must be considered in estimating the ionising power of solvents.

On solidification, hydrogen iodide shows an increase in dielectric capacity, whereas hydrogen cyanide shows a large decrease, the value for the liquid being about 100.

H. M. D.

Relation between Composition and Conductivity in Solutions of Meta- and Ortho-phosphoric Acids. EDMUND B. R. PRIDEAUX (*Trans. Faraday Soc.*, 1909, 5, 37—44).—The question as to what happens when vitreous meta-phosphoric acid or phosphoric oxide is dissolved in water has been studied by different investigators, and a review of the evidence shows that probably pyrophosphoric acid is not formed as an intermediate product. A consideration of the results of Sabatier (*Ann. Chim. Phys.*, 1899, [vi], 18, 409) led the author to the conclusion that the process is mainly one of hydration, and it was thought that a study of the electrical conductivity of the changing solution would throw light on the subject.

The aqueous acid was prepared by adding pure phosphoric oxide to cold water, and contained 0.24 equivalent per litre. The amounts of meta- and ortho-phosphoric acids were determined from time to time by titration with alkali, using methyl-orange and phenylphthalein respectively as indicators; the electrical conductivity of the changing solution decreased at first slowly, then more rapidly, and then more slowly again. The solution when first made contains about 75% of the total dissolved acid as meta-phosphoric acid, the remainder being the ortho-acid; there is no evidence of the formation of pyrophosphoric acid. The metaphosphoric acid exists as both polymerised and simple molecules, the proportions of which may vary widely in different solutions of the same total concentration. The changes which take place in the solution are due to depolymerisation of the metaphosphoric acid, a process which is practically complete in twenty-four hours, and

hydration of the meta- to ortho-phosphoric acid. This last change takes place very slowly, not being complete in fourteen days at 25°.

T. S. P.

Effect of Temperature and Dilution on the Conductivity of Organic Acids in Aqueous Solution. GEORGE F. WHITE and HARRY C. JONES (*Amer. Chem. J.*, 1909, 42, 520—541).—This investigation was undertaken in view of the fact that a systematic study of the conductivity and dissociation of organic acids with special reference to the effect of temperature and dilution has not hitherto been carried out. A brief review is given of previous work on conductivity and dissociation at various temperatures, and particularly that dealing with organic acids.

Jones and West (Abstr., 1905, ii, 794) and Jones and Jacobson (Abstr., 1908, ii, 1011) have shown that for a large number of substances between 0° and 35° dissociation decreases with rise of temperature, and Noyes (Abstr., 1904, ii, 226) has found that the same is true at high temperatures. It has also been stated by Jones and Jacobson (*loc. cit.*) that the molecular conductivity of electrolytes in aqueous solution increases as a parabolic function of the temperature, and this is explained on the hypothesis that all electrolytes in aqueous solution are more or less hydrated.

A study has been made of the conductivity of aqueous solutions of acetic, propionic, *n*-butyric, phenylacetic, malonic, succinic, *o*-phthalic, benzoic, salicylic, gallic, cinnamic, *o*- and *p*-aminobenzoic, and sulphanilic acids, the measurements being made at temperatures between 0° and 35°, and at dilutions ranging from $N/2$ to $N/2048$. The dissociation at 25° was calculated in each case by means of Ostwald's values for the conductivity at infinite dilution. The results are tabulated.

The dissociation constants of the dibasic acids, namely, malonic, succinic, and *o*-phthalic acids, increase considerably from the dilution $N/1024$ to that of $N/2048$, and it is therefore between these dilutions that the second hydrogen atom begins to dissociate.

The increase with dilution of the constants of *o*- and *p*-aminobenzoic acids is probably due to the breaking down of the inner salts on dilution.

The temperature-coefficients of nearly all the acids decrease regularly with dilution and rise of temperature, and are generally small and of the same order of magnitude; this is in accordance with the hydration theory. The viscosity of the medium is the chief factor which influences increase of conductivity of acids with rising temperature. Sulphanilic and *o*- and *p*-aminobenzoic acids differ from the other acids in having very large percentage temperature-coefficients which decrease with dilution. Moreover, the conductivities of sulphanilic and *o*-aminobenzoic acids are not parabolic functions of the temperature. The temperature-coefficients of these three acids, expressed in conductivity units, increase greatly with rise of temperature. These peculiarities are probably due to the fact that these three acids, having both basic and acidic groups, form internal salts which break down as

the temperature rises, and the free acids conduct more readily than the salts themselves. E. G.

Transport Number of Hydrochloric Acid. ERNST H. RIESENFELD and B. REINHOLD (*Zeitsch. physikal. Chem.*, 1909, 68, 440—458).—The sources of error in the determination of transport numbers by Hittorf's method are discussed, and it is shown that for the attainment of an equal degree of accuracy with solutions of different concentration, the diameter of the transport apparatus must vary as the cube-root of the concentration. An improved form of transport apparatus is described, the special feature of which is that the anode and cathode compartments are bent several times; this arrangement has been found very efficient for diminishing alterations in the intermediate layers. The apparatus was of the same diameter throughout.

With this apparatus the transport number, n , of the anion in solutions of hydrochloric acid of intermediate concentration has been determined at 18° with the following results: 0.977*N*, $n=0.155$; 0.452*N*, $n=0.155$; 0.104*N*, $n=0.161$. G. S.

Determination of Transport Numbers from *E.M.F.* Measurements in Solvents which are only Partially Miscible with Water. ERNST H. RIESENFELD and B. REINHOLD (*Zeitsch. physikal. Chem.*, 1909, 68, 459—470).—The *E.M.F.* of concentration cells, made up with two non-miscible solvents, is calculated for the general case when the concentration in the second solvent has any value whatever. In two cases: (1) when the concentration in the second solvent is small; (2) when the two solvents are in partition equilibrium, the *E.M.F.* of the cell is represented by the simple expression $E = RTn_2 \log C_1/C_2$ [1], where n_2 is the transport number of the anion of the binary electrolyte in the second solvent, and C_1 and C_2 are the concentrations of the electrolyte in the first solvent in contact with the anode and cathode respectively.

From measurements of the *E.M.F.* of cells of the second type, the transport numbers of the anions of potassium chloride and bromide in phenol as second solvent have been determined. Phenol was brought into partition equilibrium with *N*/10 (Phenol I) and *N*/100 (Phenol II) aqueous solutions of the electrolyte by shaking in a separating funnel for some time, and a cell of the following type: electrode | *N*/10 aqueous solution | Phenol I | Phenol II | *N*/100 aqueous solution | electrode, was then constructed and its *E.M.F.* measured. The electrodes were reversible with regard to the cation.

From the results, the transport number of the anions in phenol was calculated by equation [1], and both salts gave the same value, 0.439. A direct determination by Hittorf's method of the transport number of the anion in potassium chloride dissolved in phenol gave the value 0.475, which is probably less accurate than the above value.

For all the alkali salts examined, the relative velocity of the anion with reference to that of the cation is less in phenol than in water.

G. S.

Relative Rates of Migration of Ions in Aqueous Solution.

I. ROBERT B. DENISON (*Trans. Faraday Soc.*, 1909, 5, 165—171).—The transport-numbers of the chlorides, bromides, and iodides of sodium, potassium, ammonium, rubidium, cesium, magnesium, calcium, strontium, and barium have been determined by the method of direct observation of moving ionic boundaries, using the apparatus previously described by the author in conjunction with Steele (Abstr., 1906, ii, 68, 329). The concentrations of the solutions were 0.1 to 0.02 normal. The ionic mobilities in cm./sec. per volt./cm. are also calculated, together with the molecular conductivities. T. S. P.

Thermo-electric Forces of Certain Metallic Oxides and Sulphides. J. WEISS and J. KOENIGSBERGER (*Physikal. Zeitsch.*, 1909, 10, 956—957).—The thermo-electric forces obtained by combination of certain oxides and sulphides with metallic copper have been measured. The temperatures of the hot and cold junctions, 80° and 20° respectively, were measured by small thermo-elements in direct contact with the junctions. Considerable care was taken to obtain perfectly homogeneous material for the experiments, for it is to the lack of homogeneity that the discrepant values obtained by previous observers are attributable. Values of the thermo-electric potential difference per 1° difference of temperature are recorded. H. M. D.

Very Short Electromagnetic Waves. Anomalous Reflexion and Dispersion of Liquids. H. MERZYNG (*Compt. rend.*, 1909, 149, 981—983).—Maxwell's relation, that the square of the refractive index is equal to the specific inductive capacity (dielectric constant), does not hold for many substances, especially for liquids. There should exist a region of transition between that where the index of refraction is defined optically and that where it is defined electrically for very long waves. Drude (Abstr., 1897, ii, 438, 537) used electrical waves of $\lambda = 75$ cm., and Cole of $\lambda = 5$ cm. The author uses waves of $\lambda = 4.5$ cm., and determines the index of refraction (n) of a liquid by measuring the angle of incidence (i) of the rays and the ratio (R) between the intensities of the reflected and direct waves, making use of Fresnel's equation: $\sqrt{R} = (\sqrt{n^2 - \sin^2 i} - \cos i) / (\sqrt{n^2 - \sin^2 i} + \cos i)$. The dielectric constant (D) is then calculated from the refractive index, assuming that $D = n^2$. The results are as follows, and at the same time the dielectric constant (D_{opt}) calculated from the optical refractive index and that (D_{el}) calculated from the refractive index for long electrical waves are given for comparison:

Liquid.	D .	D_{opt} .	D_{el} .
Glycerol	16.8	2.1	56
Methyl alcohol	29.4	1.8	32—33
Amyl alcohol	3.31	1.9	16
Acetic acid	3.5	1.9	9.7
Aniline	4.36	2.5	7.4
Ethyl ether	3.26	1.9	4.25

T. S. P.

Conditions Necessary for Maintaining Platinum in a State of Incandescence in the Interior of a Bunsen Burner. JEAN MEUNIER (*Compt. rend.*, 1909, 149, 924—926).—The author has

shown previously that the property which platinum possesses of remaining incandescent in a mixture of air and coal gas depends on the composition of the mixture (Abstr., 1909, ii, 311). He now shows that if a platinum wire is first cleaned with hydrochloric acid and then heated, it loses the property of remaining incandescent; if, however, it is passed between the fingers it regains that particular property because it takes up saline matter from them. This saline matter can be removed from the fingers by washing them in acidified distilled water, but not with soap and water.

Below a certain limit, the duration of the incandescence depends on the weight of substance deposited on the wire. From experiments with ordinary water containing 1.070 grams of total solids per litre, the relation between the duration of incandescence and the weight of substance deposited on the wire was determined. It was found, for example, that if the incandescence persisted for three minutes, the weight of substance deposited on the wire was 6/10,000 mg.

Thus platinum itself is not responsible for the incandescence, but rather the saline matter which is on its surface. T. S. P.

Theoretical Cooling Curves of Binary Mixtures. ÉTIENNE RENGADE (*Compt. rend.*, 1909, 149, 782—785).—The cooling curve of a pure substance consists of three practically straight lines, namely, the liquid cooling curve, the constant temperature during solidification, and the solid cooling curve. In the case of a mixture, the middle curve, that is, the cooling curve between the liquidus and the solidus, can be approximately calculated as follows. Assuming that *A* and *B* retain their specific heats unchanged in presence of each other, that the latent heat of solidification of *A* is unaffected by *B* in the mother liquor, and that the lowering of the freezing point of *A* is strictly proportional to the concentration of *B*, the author calculates that $\lambda dt = (1-s)[(1-C_1)m_1 + C_1m_2]dy + sm_1'dy + Lds$, where *s* molecules of *A* are deposited in time *t*, during which the freezing point falls by *y*^o and the concentration of *B* increases from *C* to *C*₁; *m*₁, *m*₂ represent the specific heats of liquids *A*, *B*, and *m*₁' of solid *A*. This expression, simplified by assuming that *m*₁, *m*₂, and *m*₁' are all equal, yields on differentiating: $(m_1y - \lambda t + L)(Ky + C) = CL$.

The curve to this equation is an hyperbola having as asymptotes the lines $m_1y - \lambda t + L = 0$ and $Ky + C = 0$, the latter being parallel to the axis of *t*.

The cooling curve is a straight line to the point [0,0], where solidification begins with separation of *A*, and then follows the hyperbola. If *C* = 0, that is, if *B* is absent, the hyperbola reduces to its asymptotes, namely, a right line parallel to the axis of *t* during solidification and a right line representing the cooling of the solid *A*. Cooling curves determined experimentally in the author's automatic apparatus (Abstr., 1909, ii, 573) are in complete accord with the above analytical equations.

Other cases, where *m*₁, *m*₂, and *m*₁' are not equal, are also discussed. R. J. C.

Theoretical Form of the Cooling Curves of Binary Mixtures The Case of Solid Solutions. ÉTIENNE RENGADE (*Compt. rend.*, 1909, 149, 990—993).—Making use of the same assumptions as those employed in a previous paper (preceding abstract), the author deduces an equation for that part of the cooling curve of a binary mixture lying between the point of initial separation of the solid and the point of complete solidification, assuming that a solid solution is formed. The resulting curve is a hyperbola, one of the asymptotes being fixed and inclined to the time-axis, whereas the other asymptote is movable, but always parallel to the time-axis. A consideration of the curve shows that the point of complete solidification is always less marked than the point where the solid commences to separate. Other relations are also deduced which depend on the latent heats of fusion of the two components.

T. S. P.

Superheating of Crystals. GUSTAV TAMMANN (*Zeitch. physikal. Chem.*, 1909, 68, 257—269).—The paper contains a theoretical discussion of the conditions under which a crystal can be superheated while it is melting. Such superheating is always possible when the flow of heat to the crystal is sufficiently great, and can be realised the more easily the smaller the maximum linear velocity of crystallisation. It is, however, only during melting that crystals can be heated above the melting point.

These considerations have been tested by supplying heat to three substances of different crystallisation velocity, naphthalene, betol (β -naphthyl salicylate), and dextrose, and determining the rate of change of temperature with the time. For naphthalene there is a definite halt at the melting point, corresponding with the relatively great velocity of crystallisation, but for betol and dextrose, the velocity of crystallisation of which is slow, there is a rise of temperature during melting, so that the crystals of the latter two substances can be superheated.

The melting point of substances which do not melt sharply can in many cases be determined by a dilatometer method. The melting point of levulose determined in this way is 91° , but the results are complicated by the fact that this substance undergoes some change when heated in the neighbourhood of its melting point.

It might be supposed that the extremely slow rate of crystallisation of many fused sugars is connected with molecular complexity, but molecular weight determinations by the cryoscopic method lend no support to this suggestion.

G. S.

Melting-point Apparatus which can also be Used for the Determination of Solubilities with small Quantities of Substance. H. STOLTZENBERG (*Ber.*, 1909, 42, 4322—4324).—Two new forms of apparatus are described, (a) for temperatures up to 350° , and (b) for low temperatures down to -60° . The apparatus is similar in principle to Thiele's apparatus (*Abstr.*, 1907, ii, 330), but the circulation is brought about, not only by heating or cooling a spiral side-tube, but also by bubbling carbon dioxide through it. For

solubility determinations, a sieve containing the solid is hung in the tube which contains the thermometer; owing to the rapid circulation of the liquid, a saturated solution is rapidly obtained. T. S. P.

Iodine as a Cryoscopic Solvent. F. OLIVARI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 384—389).—The molecular depression of the freezing point of iodine, determined by means of arsenious iodide, lead iodide, stannic and mercuric iodides, has the mean value 213 (compare Timmermans, *Abstr.*, 1906, ii, 429; Beckmann, *Abstr.*, 1909, ii, 642); van't Hoff's equation gives the value 13.88 for the latent heat of fusion of iodine in place of the number, 11.7, employed by Timmermans.

Determination of the molecular weights in freezing iodine of a number of hydrocarbons, halogen derivatives, ketones, anhydrides, and acids, which can be separated unchanged by removing the iodine by means of thiosulphate, gives the following results: (1) in general, the molecular weights are greater than the theoretical numbers, and increase rapidly with the concentration; (2) this increase becomes more and more rapid on passing from the hydrocarbons towards the acids; (3) the molecular weights at infinite dilution, determined by extrapolation, approach the normal values for the hydrocarbons and their halogen derivatives, but are still greater, by varying amounts, than the theoretical values for succeeding compounds in the passage towards the acids.

These anomalous values are due to: (1) the fact that, owing to the high density of iodine (about 4), weight concentrations in proportion to the numbers 1, 2, 3, etc., correspond with volume concentrations in proportion to 4, 8, 12, etc., so that the concentrations rapidly attain values to which the fundamental cryoscopic laws are inapplicable; (2) the varying degree of polymerisation of the dissolved substance, and (3) the formation of additive, hydrate-like compounds of iodine with the liquid in which it is dissolved (compare Beckmann, *Abstr.*, 1893, ii, 382; 1907, ii, 340; Vaubel, *Abstr.*, 1901, ii, 446; Hantzsch and Vagt, *Abstr.*, 1903, ii, 8; Lachmann, *Abstr.*, 1903, ii, 283; Strömholm, *Abstr.*, 1903, ii, 644; Hildebrand and Glascock, *Abstr.*, 1909, ii, 225).

The molecular weight will be greater than the normal if the substance R forms a complex I_nR_n , in which n is greater than 1. If the complex dissociates according to the scheme: $I_nR_n \rightleftharpoons I_{n-1}R_{n-1} + R$, $I_nR_{n-1} \rightleftharpoons I_{n-2}R_{n-2} + R$, etc., increase of the concentration of R will favour equilibria corresponding with higher molecular weights (compare also Beckmann, *Abstr.*, 1909, i, 652).

The molecular weight of tetramethylammonium iodide in freezing iodine is found to be 257.4—273 (200.9); of potassium iodide, 229.6—240.5 (166); of calcium iodide, 1043—1165 (293.8), and of strontium iodide, 900.6—1077 (341.34). Iodine solutions of sulphur containing 0.8951—2.36% of sulphur give molecular weights corresponding with S_8 , more dilute solutions giving lower values (compare *Abstr.*, 1909, ii, 37); these results are not in accord with the results of thermal analysis of mixtures of sulphur and iodine, which indicated partial isomorphism between the two elements (compare Ephraïm, *Abstr.*, 1908, ii, 581). The molecule of selenium in iodine solution is of

the order of magnitude Se_3 (compare Abstr., 1909, ii, 805). Tellurium combines directly with fused iodine; measurements made with a sample of 94% tellurium give the molecular weights 159—171.2 ($\text{Te} = 127.6$).

T. H. P.

Vapour Pressures at Low Temperature. LUIGI ROLLA (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 365—373).—For measuring vapour pressures at low temperatures, the author employs an apparatus devised by Nernst, which was graduated by a manometer containing paraffin oil of known density. That the apparatus gives trustworthy results is shown by measurements of the vapour pressure of ice at the temperatures -43.5° , -38.5° , and -30° , the results obtained being in good agreement with those of Scheel and Heuse (Abstr., 1909, ii, 643), who employed a Rayleigh manometer.

For naphthalene, the vapour pressure is found to be 0.00878 mm. of mercury at 0° , and 0.0381 mm. at 15.0° (compare Allen, *Trans.*, 1900, 77, 400). The values calculated by means of Nernst's formula: $\log_{10} p = -\lambda_0 T/4.571 + 1.75 \log T - \epsilon T/4.571 + C$ (in which p indicates the vapour pressure in atmospheres at the absolute temperature T , and λ_0 , ϵ , and C are constants) are 0.0083 mm. at 0° and 0.0396 mm. at 15° .

For iodobenzene, the values obtained are: 0.0189 mm. at -25.8° , 0.0310 mm. at -19.8° , 0.0701 mm. at -11.5° , and 0.0887 mm. at -8.1° . From the first of these values, that of Young (*Trans.*, 1889, 55, 486) for 160° and the value at 67.46° obtained by interpolation, the author calculates the constants of Nernst's formula (*vide supra*), and from the latter the vapour pressures at temperatures varying from -25.8° to 200° , the calculated values being in good agreement with the author's and Young's results.

Similar calculations for bromobenzene give numbers in good accord with the experimental values of Young (*loc. cit.*) and the author, Nernst's formula being thus verified. The author's values are: 0.0956 mm. at -26.1° , 0.164 mm. at -20.0° , 0.186 mm. at -18.5° , and 0.191 mm. at -17.7° .

T. H. P.

Critical Phenomena of Solution. J. TIMMERMANS' (*Bull. Soc. chim. Belg.*, 1909, 23, 433—451. Compare Abstr., 1909, ii, 981).—From a consideration of the critical solution phenomena exhibited by different pairs of liquids, it is shown that these can be divided into three groups. The characteristics of one of these groups have been examined in detail with reference to the form of the critical solution curves on the pressure-temperature diagram. For a particular isothermal, three critical points may be realised as the pressure is gradually raised. This is a consequence of the retrogressive character of the pressure-temperature curve.

H. M. D.

Recent Investigations in Thermochemistry. THEODORE W. RICHARDS (*J. Amer. Chem. Soc.*, 1909, 31, 1275—1283).—An account of recent advances in the methods of thermochemical investigation.

E. G.

Alteration of Compressibility with the Softening of an Amorphous Substance. ALFRED DENNYS COWPER and GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1909, 68, 281—288).—A special form of apparatus for determining compressibilities is described and figured. It consists of a cylindrical vessel, in which the substance to be examined is placed; the vessel is connected on one side with a manometer and on the other with a steel cylinder, in which a well-fitting ebonite piston moves. The distance through which the piston has to be moved in order to alter the pressure from p_1 to p_2 is measured, and from this and the constants of the apparatus the compressibility is calculated.

In practice, it is only for such viscous liquids as castor oil that the filtration past the piston does not cause serious error at high pressures, and measurements have therefore been made with castor oil alone, and when part of the oil is displaced by crystalline and by amorphous dextrose respectively. The coefficients of compressibility of castor oil, at temperatures from 25° to 100°, and at pressures of 250—2000 kilog./cm.², are given in tabular form, and the coefficients for crystalline and amorphous dextrose are given between the same limits. Between 25° and 100° and from 250—1500 kilog.-pressure, the coefficient of compressibility of crystalline dextrose is independent of temperature and pressure, and is 76×10^{-7} when referred to the volume at 25° and 1 kilog.-pressure. The compressibility of amorphous dextrose is about double that of the crystalline form; it increases somewhat with increasing temperature, and diminishes with increasing pressure. G. S.

Connexion of Surface-tension with the Internal Pressure and van der Waals' Constants a and b . ISIDOR TRAUBE (*Zeitsch. physikal. Chem.*, 1909, 68, 289—294).—In connexion with Walden's series of papers on the same subject (compare Abstr., 1909, ii, 119, 123, 547), the author maintains his priority in some points, and supplements his own and Walden's work by further values of a and b and of internal pressures. The results show that the ratio of a to b is approximately the same for all substances, and, further, that the sum of the square roots of the atomic weights is proportional to the sum of the atomic volumes. G. S.

Viscosity of Water. RICHARD HOSKING (*J. Roy. Soc., New South Wales*, 1908, 42, 34—56; 43, 34—38).—In earlier measurements (compare Abstr., 1900, ii, 336) of the viscosity of water by the efflux method, the rate of flow of liquid in the capillary tube was made so small that the kinetic energy correction was of relatively small magnitude. New experiments have been made in which the rate of flow was increased, with the object of testing the formula by means of which correction was made for the kinetic energy. As the pressure determining the flow is increased, there appears to be an abrupt change in the numerical factor contained in the kinetic energy reduction term, or a change in the nature of the flow. Consistent values for the viscosity at 50° were, however, obtained, until the kinetic energy correction was as high as 60%. The absolute values of the viscosity

of water at 0°, 25°, and 50° are 0.01793, 0.00893, and 0.00550 respectively. It is estimated that the probable error of these values is only 0.1%.

The measurements of the viscosity were extended up to 100°. Values representing the viscosities and the relative fluidities are tabulated for every 5° between 0° and 100°. For temperature intervals of 25° the viscosity data can be accurately represented by formulæ of the type $\eta_t = \eta_0 / (1 + k_1 t + k_2 t^2)$. A less exact representation over the whole range of temperature is afforded by the formula

$$\eta_t = 9.185 / (46.694 + t) \times 1.6232.$$

H. M. D.

Viscosity of Solids at Low Temperatures. CHARLES E. GUYE and V. FREDERICKSZ (*Compt. rend.*, 1909, 149, 1066—1069).—Guye and Mintz have investigated previously the effect of rise of temperature on the viscosities of certain metals (Abstr., 1908, ii, 930), and this work has now been extended to the investigation of the effect of lowering of temperature.

Silver, aluminium, iron, gold, magnesium, and quartz were each examined at 100°, 50°, 0°, -80°, and -196°. The first three showed decreases in viscosity with lowering temperature, but probably the viscosity does not become zero at -273°. Magnesium and gold show decreases in viscosity until -80° is reached, but at -196° exhibit a considerable increase. The modulus of elasticity augments with fall in temperature for the metals, but the reverse is the case with quartz.

T. A. H.

Mechanism of the Adsorption ("Sorption") of Hydrogen by Carbon. JAMES W. MCBAIN (*Phil. Mag.*, 1909, [vi], 13, 916—935; *Zeitsch. physikal. Chem.*, 1909, 63, 471—497).—Experiments have been made on the adsorption of hydrogen by cocoa-nut charcoal at the temperature of liquid air, which show that the process is of dual character, consisting in a surface condensation and the formation of a solid solution accompanied by diffusion into the interior of the carbon.

By suitable manipulation a sample of carbon can be prepared which contains a considerable amount of hydrogen in a state of solid solution, but is almost destitute of hydrogen condensed on the surface. This condition is attained by suddenly exposing to low pressure carbon which has been previously saturated by long contact with hydrogen.

The fact that the surface condensation is nearly instantaneous, whereas the diffusion process requires several hours, enables the two phenomena to be separately examined, and various methods for the isolation of the two effects are described.

The true solubility (as distinguished from the surface condensation) of hydrogen in cocoa-nut carbon at the temperature of liquid air varies with the square root of the pressure, indicating that the dissolved hydrogen is split up into simple atoms. The solubility amounts to 4 c.c. (corr.) of hydrogen per gram of carbon when the pressure is 19 mm. of mercury. The true solubility at the ordinary temperature is less than one hundredth as great.

The term "sorption" is suggested to embrace all adsorption and occlusion phenomena.

H. M. D.

Relations between the Critical Constants and Certain Quantities connected with Capillarity. R. D. KLEEMAN (*Phil. Mag.*, 1909, [vi], 18, 901—908. Compare Abstr., 1909, ii, 645, 869).—A further relationship between the pressure, density, and molecular weight of liquid substances is deduced. This is found to be satisfied by a large number of organic compounds, but not by water or ethyl alcohol, and the abnormal behaviour of these is attributed to molecular association. H. M. D.

Kinetic Interpretation of Osmotic Pressure. M. M. GARVER (*J. Physical Chem.*, 1909, 13, 679—690).—A hypothesis is put forward to explain the general properties of solutions. The addition of a foreign non-volatile substance to a pure solvent is supposed to have the effect of narrowing the range of the velocities of the molecules of the solvent.

Although therefore the average molecular energy of translation will depend on the absolute temperature, there will be a smaller proportion of molecules which have exceptionally high or low velocities in a solution as compared with the proportion in the pure solvent. On the basis of this hypothesis, the depressed vapour tension of solutions and the phenomena of isothermal distillation, osmosis, and diffusion can be easily interpreted.

The osmotic transport of the solvent through a semipermeable membrane can be explained equally readily whether it be assumed that the interstices of the diaphragm are occupied only by the vapour of the solvent or that the solvent actually penetrates and comes into contact with the solution on the further side of the membrane. H. M. D.

Osmotic Pressure of Colloids. I. Function of Electrolytes in the Dialysis of Colloids. WILHELM BILTZ and ARVED VOS VEGESACK (*Zeitsch. physikal. Chem.*, 1909, 68, 357—382).—A special form of osmometer is described, in which the membrane consists of a collodion film deposited on a perforated frame of platinum. The upper part of the arrangement is a glass vessel, which is firmly fixed below to the platinum frame, and is provided with a narrow side-tube, which acts as a manometer. Through the upper part of the glass vessel passes a stirrer, driven by an electro-magnet. There are also arrangements by which the electrical conductivity of the solutions outside and inside the cell can be measured. The whole arrangement was placed in a thermostat at 25°. Measurements were made with benzopurpurine, night-blue, ferric and zirconium hydroxides, and tungstic acid. The general result of the observations was that in no case were equilibrium pressures obtained.

A solution of benzopurpurine was dialysed twenty days to free it, as far as possible, from electrolytes, and then placed in the osmometer. After six hours, the osmotic pressure was 10 mm. of water; after ten hours, 10.66 mm., and then it gradually diminished, until in twelve days it had fallen practically to zero. It was observed that immediately after the stirrer was started, the pressure always rose a little and this is ascribed to the mixing of the solution in the upper glass

part of the manometer with the lower part, which had gradually become poorer in electrolytes by diffusion through the membrane. When sodium sulphate is added in equivalent amount to both outer and inner liquid, the osmotic pressure is very slight. Further, when undialysed benzopurpurine is used in the osmometer, and a little sodium sulphate is added to the outer water, in course of time the conductivity becomes equal outside and inside, and there is practically no osmotic pressure. The other colloids gave similar results.

The gradual fall in the osmotic pressure is due mainly to dialysis of the electrolyte, but partly also to a gradual increase in the size of the colloidal particles. This explanation has been confirmed by experiments with dilute solutions of sodium sulphate and of night-blue respectively. In the latter case, in the absence of stirring, a false equilibrium was obtained, the tendency to rise being balanced by the dialysis of the electrolyte.

Better results should be obtained by using the filtrate from the colloidal solution as outer liquid (Duclaux), but it is not certain that the former represents the unaltered intermicellar liquid. G. S.

Influence of Substances in Solution on the Velocity of Crystallisation and the Crystal-habit of Potassium Sulphate. W. WENK (*Zeitsch. Kryst. Min.*, 1909, 47, 124—162).—Inorganic salts (various salts of potassium and sodium), added to a solution of potassium sulphate, exert a marked influence on the velocity of crystallisation of the latter salt, the growth being increased in some cases and retarded in others. Since the viscosity of the solution is not affected by these additions, it follows that the velocity of crystallisation is not dependent on diffusion; and it appears to be rather connected with adsorption and surface-tension. Organic colouring matters in the solution have a still more marked influence on the velocity of crystallisation, and they further produce an alteration in the habit of the crystals, and the colouring matter is adsorbed. L. J. S.

Isomerism and Polymorphism. ANDREAS FÖCK (*Ber.*, 1909, 43, 4527—4531).—The different crystal forms of polymorphic modifications are attributed to external and internal influences. The former include pressure, temperature and volume, and it is well known that the range of existence of the various polymorphic forms is sharply bounded by these factors. The internal influences are afforded by the configuration of the molecule, including the arrangement, position, and motion of the atoms. Alteration in pressure or temperature brings about an alteration in configuration. In solids these parallel changes are not continuous, but take place in jerks; in liquids and solutions probably both changes are continuous. In the case of an amorphous solidification, all the various configurations of the molecule present remain intact. In the various cinnamic acids, it is suggested that a slight difference in the chemical molecule is, to some extent, associated with the isomerism. E. F. A.

Preparation of Colloidal Solutions by the Disintegration of Metals by Ultra-violet Light. THE SVEDBERG (*Ber.*, 1909, 42, 4375—4377).—The metal, from which the colloidal solution is to be

formed and the surface of which has been freed from oxide, is placed in a flat dish, covered with the dispersion medium, and submitted to the action of the ultra-violet light from a Heraeus quartz mercury lamp placed a few centimetres above the liquid. After a few minutes the latter, when examined in the ultramicroscope, shows the characteristic properties of a colloidal solution.

Silver, copper, tin, and lead readily give colloidal solutions in this way, whereas platinum, aluminium, and cadmium do not. With water as the dispersion medium, lead gives a milky liquid, probably containing colloidal lead hydroxide, in five minutes; with alcohol in the place of water, a colloidal metal solution is obtained in the same time. Experiments with lead and silver in water, ethyl alcohol, isobutyl alcohol, ethyl ether, acetone, ethyl acetate, and amyl acetate showed that the number and size of the colloidal particles may vary very much, and that the disintegration depends on the nature of the dispersion medium. It was possible to produce sols which contained very small particles of very uniform size, these particles being in brisk Brownian movement.

T. S. P.

Phase Rule. JOSEPH A. MULLER (*Compt. rend.*, 1909, 149, 1079—1080).—A reply to Boulouch (Abstr., 1909, ii, 802) maintaining the validity of the author's method of deducing the relationship between the number of substances and phases of a system in equilibrium (Abstr., 1908, ii, 466).

T. A. H.

Photo- and Electro-chemical Equilibria. ANDREAS SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 356—359).—From a consideration of the equilibria in systems which are capable of absorbing light energy and electrical energy, the author is led to the view that equilibria will be established at the ordinary temperature which correspond with higher temperatures in the absence of these other forms of energy. In this connexion, reference is made to the special cases of the dissociation of hydrogen sulphide, hydrogen selenide, hydrogen iodide, the hydrides of phosphorus, arsenic, and antimony, and also of carbon dioxide.

H. M. D.

Temperature-coefficient of Chemical Reaction Velocities.
IV. The Velocity Isochore of Gas Reactions, its Connexion with that of the Reactions of Free Atoms, with Applications. MAX TRAUTZ (*Zeitsch. physikal. Chem.*, 1909, 68, 295—315. Compare Abstr., 1909, ii, 651).—A theoretical paper. A general equation, independent of the validity of the gas laws for the vapours of the reacting substances, is deduced for the velocity of gas reactions. Contrary to the former method of deduction, the heat developed in the reaction is partitioned out according to the intermediate reactions to be assumed on chemical grounds, and Nernst's thermodynamic law is employed. The equation is applied to the experimental data for the influence of temperature on the decomposition and formation of hydrogen iodide, and on the decomposition of nitric oxide and of hydrogen phosphide, and is shown to be in satisfactory accordance with the results.

G. S.

Rate of Evolution of Gases from Homogeneous Liquids. VICTOR H. VELEY (in part, with JOHN C. CAIN) (*Trans. Faraday Soc.*, 1909, 5, 1—9. Compare *Trans.*, 1883, 43, 370; 1903, 83, 736; *Abstr.*, 1903, ii, 641, etc.).—Utilising the results previously obtained by himself and other workers, the author has studied the conditions of the evolution of gases from liquids in which chemical changes are taking place, with especial reference to the degree of supersaturation, which, according to the author, appears to have been greatly over-estimated. The reactions considered are: (1) carbon monoxide from formic and sulphuric acids, (2) nitrogen from ammonium nitrite, (3) oxygen from hydrogen peroxide solutions, and (4) nitrogen from the decomposition of diazonium salts by water.

The amounts of gases retained in supersaturated solution are calculated by comparing the volumes which were actually evolved and those which would have been obtained if there had been no retention (compare *Abstr.*, 1903, ii, 641). From the known solubilities of the several gases in water, the degree of supersaturation can then be determined. The values obtained vary between 8 and 12, according to the nature of the gas and the conditions of experiment.

In a few cases of the decomposition of diazonium salts, the lag factors due to certain opposing side reactions are discussed, and their effects separated from the concomitant initial delay due to gas retention.
T. S. P.

Hydrolysis and Reaction Velocity in Mixtures of Alcohol and Water. HANS EULER and BETH AF UGGLAS (*Zeitsch. physikal. Chem.*, 1909, 63, 498—510).—The degree of ionisation and of hydrolysis of certain compounds in 80 per cent. alcohol has been determined by conductivity measurements. The dissociation constants $k \times 10^5$ for salicylic acid are as follows: 1.81 at 0°, 1.86 at 18°, 1.88 at 30°, the values being about 1/50 of those in aqueous solution. As regards the hydrolysis of aniline salicylate, the non-hydrolysed fraction in *N*/10 solution is 0.73 at 0°, 0.57 at 18°, and 0.51 at 30°. From this the dissociation constant of aniline at 18° is estimated at $k = 4 \times 10^{-12}$, assuming that the ion-product for the solvent is 0.6×10^{-16} . In *N*/100 solution the sodium salt of benzaldehyde is practically completely hydrolysed, the corresponding salt of *p*-nitrobenzaldehyde to the extent of 76%, and the corresponding salt of dextrose to 47%. The latter is thus less hydrolysed in 80 per cent. alcohol than in pure water.

An attempt was made to follow the rate of neutralisation of aniline by salicylic acid at -50° by the conductivity method, but the reaction is complete within ten seconds.

Electrical conductivity measurements indicate that phenolphthalein is a dibasic acid, and this conclusion is supported by colorimetric measurements. The red colour of concentrated alcoholic solutions of phenolphthalein salts is intensified by raising and diminished by lowering the temperature.
G. S.

Hydrolysis of Salts of Amphoteric Electrolytes. HEATHER HENDERSON BEVERIDGE (*Proc. Roy. Soc. Edin.*, 1909, 29, 648—667).—The results obtained for the degree of hydrolysis of amphoteric

electrolytes by the methods depending on the measurement of the rate of catalysis of methyl acetate and that of the electrical conductivity are not in agreement. With the object of throwing light on this discrepancy, the hydrolysis of *o*-aminobenzoic acid in acid solution has been determined by these and other methods. It is found that those methods of determining the hydrolysis which depend directly on the concentration of the hydrogen ion agree fairly well with each other. Such methods examined were the catalysis of methyl acetate by the hydrochloride, and of ethyl diazoacetate by the nitrate, and the difference of potential method. Other methods involving the solubility of the amphoteric base in acid solutions of different concentrations and the partition of the base between two immiscible solvents lead to the same value. On the other hand, the more indirect methods depending on electrical conductivity and freezing-point measurements lead to different values for the degree of hydrolysis. The conclusion is drawn that these two methods cannot be used to determine the extent of hydrolytic decomposition in the case of salts of amphoteric electrolytes. The interpretation of the freezing-point and conductivity data leads to the view that there are fewer molecules in the solution of a salt of an amphoteric electrolyte than there would be in the case of a non-amphoteric substance.

H. M. D.

Atomic Weights as Mathematical Functions. F. H. LORING (*Chem. News*, 1909, 100, 281—286).—In continuation of previous work (compare Abstr., 1909, ii, 392) the elements are arranged in the order of their atomic weights according to a method already described, and the meaning of the gaps in the arrangement is further discussed. Nitrogen does not fit into the system, and it is suggested that it is made up of helium and two other unknown inactive elements, the so-called "satellite," St, atomic weight 0.27, and an element, Nt, atomic weight 9.75. The "satellite" may occur along with other elements, for example, iodine + 2 satellites = tellurium.

A further arrangement of the elements is given, the vertical columns in the table mentioned above, or the elements singly, are displaced downwards as required in order to bring chemically allied elements into horizontal alignment. If then the squares are coloured blue, red, or purple, according as the elements are basic, acidic, or neutral in character, the basic elements occupy a triangular area, the acidic ones next to them a similar area, and the elements of neutral tendency form a rectangle. Finally, where the acidic elements repeat, an approximate square is formed. A coloured table to illustrate this arrangement accompanies the paper.

G. S.

Calculation of Atomic Weights. Solution of the Equation of Condition. GUSTAV D. HINRICHS (*Compt. rend.*, 1909, 149, 1074—1076).—A graphic method of solution is described, which includes and generalises those already given (Abstr., 1907, ii, 945; 1909 ii, 653). The graph used in illustration of the method is that for 42 determinations of the ratio $\text{AgCl} : \text{Ag}$, commencing with Berzelius' first determination and ending with those of Richards (compare Abstr., 1907, ii, 679).

T. A. H.

Molecular Rearrangements. WILLIAM A. NOYES (*J. Amer. Chem. Soc.*, 1909, **31**, 1368—1374).—A discussion of recent conceptions with regard to molecular rearrangements, and particularly with reference to the nature of the forces or attractions which hold atoms together in molecules, and which also cause atoms of different molecules to react with each other. E. G.

Inorganic Chemistry.

Anodic Formation of Hydrogen Peroxide. FRANZ RICHARZ (*Ber.*, 1909, **42**, 4674—4675. Compare Riesenfeld and Reinhold, *Abstr.*, 1909, ii, 879).—The secondary formation of hydrogen peroxide at the anode has been observed by the author (*Abstr.*, 1885, 624; 1888, 12, 769). C. H. D.

Dissociation of Hydrogen Bromide and Hydrogen Iodide at High Temperatures. KURT VOGEL VON FALCKENSTEIN (*Zeitsch. physikal. Chem.*, 1909, **63**, 270—280).—The measurements were made by determining the partial pressure of the hydrogen by Lowenstein's method (compare *Abstr.*, 1906, ii, 272). The dissociation of hydrogen bromide is 0.50% at 1024°, 0.73% at 1108°, and 1.08% at 1222°; that of hydrogen iodide is 32.9% at 1022° and 37.55% at 1217°. The results, and also the fact that at the high temperatures used the halogen molecules are partly dissociated according to the equations $\text{Br}_2 \rightleftharpoons 2\text{Br}^*$ and $\text{I}_2 \rightleftharpoons 2\text{I}^*$, will be discussed in a later communication G. S.

Electric Conductivity and Density of Solutions of Hydrogen Fluoride. ERNEST G. HILL and ANNODA P. SIRKAR (*Proc. Roy. Soc.*, 1909, **A**, **83**, 130—148).—Measurements have been made of the electrical conductivity and density of mixtures of water and hydrogen fluoride ranging from the one pure substance to the other. A satisfactory conductivity cell was constructed from paraffin wax of low melting point (40.4°). The density measurements were made by weighing a lead cylinder coated with paraffin wax in the various liquids.

Curves are plotted which show the variation of the specific conductivity and of the density with the percentage composition of the solutions. These are of approximately the same type, and exhibit a well-defined maximum for a solution containing 75% of hydrogen fluoride. The curve, which is obtained when the molecular conductivity of the hydrogen fluoride is plotted as a function of the concentration, shows two distinct breaks, one at about 91%, the other between 51% and 55% of hydrogen fluoride. The former corresponds with the composition $9\text{HF} \cdot \text{H}_2\text{O}$, the latter with $\text{HF} \cdot \text{H}_2\text{O}$, and the

authors draw the conclusion that definite hydrates of this composition are present in the solutions.

From values obtained for the conductivity at 0° and 18°, the temperature-coefficient has been calculated. This is constant, and equal to 0.0125 for solutions containing less than 7.7% of hydrogen fluoride. By applying this temperature correction, molecular conductivity data for 25° are obtained. On comparison with Ostwald's numbers for dilute solutions, a satisfactory agreement is obtained at the dilution $v=4$, but for more dilute solutions the authors' numbers are much smaller than Ostwald's, the difference increasing with the dilution.

H. M. D.

Production of Ozone by Ultra-violet Light. EDMOND VAX AUBEL (*Compt. rend.*, 1909, 149, 983—985).—Bordier and Nogier (*Compt. rend.*, 1908, 147, 354) could not find that ozone was produced from the oxygen of the air by the action of ultra-violet light, although previous observers (compare Abstr., 1906, ii, 224; 1909, ii, 657) had observed its formation. Using a quartz mercury lamp as the source of ultra-violet light, the author definitely proves that ozone is produced. Instead of using water to absorb the ozone, olive oil and light petroleum were employed in the first experiments, being placed in porcelain dishes inside the large glass globe surrounding the quartz tube. After several hours' exposure, starch iodide showed the presence of ozone in these liquids. When distilled water was submitted to the action of the ultra-violet light for fourteen hours, the presence of ozone was detected by its action on a photographic plate. Starch iodide paper was turned blue in two minutes, except where it was covered with a piece of quartz, and thus prevented from coming into direct contact with the ozonised air.

T. S. P.

Boiling Point of Sulphur Corrected by Reference to New Observations on the Absolute Expansion of Mercury. HUGH L. CALLENDAR and HERBERT MOSS (*Proc. Roy. Soc.*, 1909, A, 83, 106—108).—As a result of new measurements of the expansion of mercury between 0° and 300°, it has been found necessary to add a correction factor to the result obtained for the boiling point of sulphur by Eumorfopoulos (Abstr., 1908, ii, 1029). This raises the temperature from 443.58° to 444.55°, which is in practically perfect agreement with the value previously assumed (444.53°).

H. M. D.

The Dynamic Allotropy of Selenium. HUGO R. KAUER (*Zeitsch. anorg. Chem.*, 1909, 64, 305—326).—The study of the electrical conductivity is uncertain as a means of investigating the dynamic allotropy of selenium, conductivity not being an additive property. The author has, therefore, used the specific gravity, the reciprocal of which is a strictly additive property of solid solutions. The material was purified as described by Marc in his study of selenium (Abstr., 1904, ii, 105; 1906, ii, 226, 280, 742; 1907, ii, 453).

Grey, crystalline selenium, which has not been heated above 130°, has D 4.5—4.6, whilst sublimed selenium has D 4.80. The difference is not due to the presence of amorphous selenium. After fusion, passage

of the amorphous into the crystalline form, and heating to 125° , the preparation has D 4.77. The denser form passes into a modification with D 4.77 when heated to 125° . There is thus an equilibrium, $\text{Se}_1 \rightleftharpoons \text{Se}_2$, high temperatures favouring the denser form. Exposure to the light of an arc lamp, or even to bright diffused light, the selenium being enclosed in a dilatometer with alcohol, produces an increase of volume; the quantity of Se_1 is, therefore, increased by illumination. The changes in the electrical conductivity are explained on the assumption that Se_1 and Se_2 form solid solutions, and also form a compound giving a diagram of the same form as is obtained from mixtures of bromine and iodine (Terwogt, Abstr., 1906, ii, 15) and alloys of magnesium and cadmium (Grube, Abstr., 1906, ii, 355). The conductivity has then two minima, with a sharp cusp on the curve corresponding with the compound. The anomalous behaviour of specimens cooled from 200° is explained as being due to the combined action of light and heat in altering the equilibrium, and also in changing the velocity with which equilibrium is attained.

The conclusion is drawn that all phases of selenium contain Se_1 and Se_2 , whilst red, crystalline selenium is labile, and may perhaps also occur in two modifications.

C. H. D.

Coefficients of Absorption of Nitrogen and Oxygen in Distilled Water and Sea-Water, and of Atmospheric Carbon Dioxide in Sea-Water. CHARLES J. J. FOX (*Trans. Faraday Soc.*, 1909, 5, 68—86).—The apparatus used for determining the coefficients of absorption of nitrogen and oxygen was a modified form of Estreicher's adaptation (Abstr., 1900, ii, 205) of Ostwald's apparatus. The pressure used could be varied at will, whereas Estreicher's had to make the measurements at exactly atmospheric pressure. Special precautions were taken to free the water from dissolved air, and it is suggested that the method used by Estreicher was not satisfactory, so that his values for the absorption coefficients for argon and helium may be respectively 0.2 to 5% and 0.5 to 10% too low.

Two series of measurements of the solubility of atmospheric nitrogen in distilled water between 0° and 50° were made. A correction had to be applied, due to the different solubilities of nitrogen and argon and the variation of the partial pressures with temperature. The relation between the absorption coefficient (α_x) and the temperature is given by the formula $1000\alpha_x = 22.998 - 0.5298t + 0.0091962t^2 - 0.00006779t^3$. In the case of oxygen the formula obtained was $1000\alpha = 49.239 - 1.3440t + 0.28752t^2 - 0.0003024t^3$. These formulae give the following values for gas absorbed in c.c. per litre.

	0°	10°	20°	30°	40°	50°
Nitrogen...	23.00	18.54	15.51	13.55	12.15	11.02
Oxygen ...	49.24	28.37	31.14	26.65	23.30	20.95

Determinations were also made on sea-waters of four different salinities. These values were then combined with those obtained for distilled water, and formulae obtained connecting the absorption coefficient, temperature, and salinity (chlorine-content) of the sea-water for nitrogen and oxygen at the partial pressures they have in air.

Tables are then given showing the amount of nitrogen (containing argon) and oxygen (in c.c.) absorbed by 1000 c.c. of sea-water from a free dry atmosphere of 760 mm. pressure at temperatures from 0° to 28°, and the chlorine content 0—20 per mille.

In the case of carbon dioxide the pressure in sea-water varies probably between 1 and 7 parts per 10,000; the total alkalinity also varies, and for the open ocean is equivalent to about 40 mg. OH per litre. The carbon dioxide pressure was determined by a modification of Pettenkofer's method. It was first of all established that the ratio of total CO_2 to total OH is rectilinear, and as a result of the law of mass action no CO_3^{--} ions are formed; all the combined carbon dioxide must be in the form of HCO_3^- . The effect of varying pressure on only one alkalinity, that selected being 40 mg. OH per litre, was then determined. From these results an interpolation formula connecting the carbon dioxide per litre of sea-water, the salinity, the alkalinity, the temperature, and the pressure was obtained, and tables of the calculated results are given.

From these tables a calculation can be made of the power of the sea to conserve the constancy of carbon dioxide in the air (compare Arrhenius, *Phil. Mag.*, 1896, [v], 41, 273). The conclusion is drawn that for the open ocean (OH = 40 mg. per litre and $t = 12^\circ$) it requires 17.6 times as much carbon dioxide to raise the carbon dioxide partial pressure as for the same volume of air; or, if a quantity of carbon dioxide is poured into the air, as, for example, by volcanic action, two-thirds will eventually be absorbed by the sea. The final equilibrium will not be attained, however, until either the insoluble carbonates on the sea-bottom or the carbon dioxide in the air have completely gone into solution in the form of HCO_3^- . The time necessary for this is not known, but it must be very important geologically.

The concentrations of the free ions, HCO_3^- and H^+ , for ocean-water are calculated to be respectively 2.24×10^{-3} and $1.6 - 2.6 \times 10^{-6}$ gram-equivalents per litre; thus sea-water is just slightly more acid than distilled water.

The paper also contains a description of the apparatus used for extracting and analysing gases dissolved in liquids.

T. S. P.

Red Phosphorus and the so-called "Hittorf's Phosphorus."
ALFRED STOCK and FRANZ GOMOLKA (*Ber.*, 1909, 42, 4510—4527). —Hittorf's phosphorus, having the high density 2.3, is the only variety, other than yellow phosphorus, which is at all well defined, the ordinary red variety being a mixture.

Hittorf's phosphorus is best prepared by heating 3 grams of pure phosphorus with 200 grams of lead in a sealed Jena glass tube, packed in sand, to 800° for forty-eight hours. The glass is broken and removed in a freezing mixture, and the lead cleaned by brushing and by washing with hydrofluoric acid. As nitric acid attacks the phosphorus, the lead is best removed by electrolysis in acetic acid containing lead. The cathode is placed at the bottom of the vessel, a clock-glass being fixed below the rod. The residue thus obtained contains some lead, mechanically dislodged from the anode, and is purified by boiling with

hydrochloric acid in an atmosphere of carbon dioxide, followed by treatment with hydrofluoric acid. The purest product still contains 1.5% of lead.

Bismuth may be used in place of lead, but it dissolves only one-fifth as much phosphorus, and the crystals obtained are less pure. The metals appear to be held in solid solution.

Only very minute quantities of Hittorf's phosphorus are obtained by sublimation. An improvement of this method is being studied.

Ordinary red phosphorus melts at 605–610°, and Hittorf's phosphorus at 620°. The product obtained by fusion in a closed tube is heterogeneous.

Hittorf's phosphorus, corrected for the dissolved lead, has D 2.31–2.33. It is much less chemically reactive than ordinary red phosphorus at high temperatures, but both oxidise slowly in the air to deliquescent products. The statement, often made, that red phosphorus is stable in air, is incorrect.

C. H. D.

Oxidation of Phosphorus. WILLEM P. JORISSEN and N. H. SIEWERTSZ VAN REESEMA (*Chem. Weekblad*, 1909, 6, 931–938. Compare Schmidt, Abstr., 1902, ii, 237; Scheuck, Mihr, and Banthien, Abstr., 1906, ii, 326; de Broglie and Brizard, Abstr., 1909, ii, 535; Riboul, *ibid.*, ii, 718; Elster and Geitel, *Physikal. Zeitsch.*, 1902, 3, 475; 1903, 4, 111, 293, 436, 457; *Ber. deut. physikal. Ges.*, 1906, 640).—The work of Elster and Geitel and of Schmidt on the oxidation of phosphorus has been repeated. The results obtained support the conclusions of Elster and Geitel, but indicate that Schmidt's statements are erroneous.

A. J. W.

Preparation of Hypophosphoric Acid. JACQUES CAVALIER and F. CORNEC (*Bull. Soc. chim.*, 1909, [iv], 5, 1058–1060).—A number of glass rods are placed across the bottom of an ordinary photographic washing dish, and on these are laid transversely, sticks of phosphorus, separated from each other by glass rods. Water is then poured into the dish until the phosphorus is half submerged. The whole is covered by a glass plate resting on a layer of cotton wadding, so that air is slowly but continuously admitted. The acid formed can be neutralised by sodium carbonate, to form sodium hydrogen hypophosphate, or the latter salt can be obtained at once by substituting a solution of sodium acetate for water in the dish. From this sodium salt, the acid is best recovered by making the lead salt by double decomposition, and regenerating the acid with hydrogen sulphide. By this process, and using a dish 13 × 18 cm., from 30 to 50 grams of sodium hydrogen hypophosphate may be obtained in five to six days.

T. A. H.

Decomposition of Water by Hypophosphites in Presence of Palladium as a Catalyst. ALEXIS BACH (*Ber.*, 1909, 42, 4463–4470).—The formation of copper hydride from sodium hypophosphite and copper sulphate takes place at the ordinary temperature, and is an example of the decomposition of water by an oxidisable substance in presence of a substance capable of combining with hydrogen. The same reaction takes place in presence of a catalyst, hydrogen being set free.

Solutions of sodium hypophosphite and palladium chloride are used, the course of the reaction being followed by measuring the volume of hydrogen evolved. The velocity of decomposition increases much more rapidly than the quantity of palladium added, the concentration of the hypophosphite being kept constant. The velocity decreases rapidly with time, and is not increased by further additions of palladium, but rises to the original value on further addition of hypophosphite. With constant palladium, the velocity increases less rapidly than the quantity of added hypophosphite. Hydrocyanic acid prevents the decomposition, or, if palladium sponge is used instead of the chloride, slowly brings it to a standstill.

The analogy of the behaviour of palladium in this case to that of a peroxidase is pointed out, both departing from the laws of chemical kinetics. The intermediate formation of an unstable palladium perhydride is assumed. C. H. D.

Phosphorescent Oxidation of Arsenic. LÉON BLOCH (*Compt. rend.*, 1909, 149, 775—777. Compare *Abstr.*, 1909, ii, 395).—The phosphorescence of arsenic at 200°, like that of sulphur and phosphorus, is accompanied by oxidation, by which arsenic trioxide is produced. As in the case of sulphur, no ionisation occurs, and there is also no formation of ozone, which is produced by both sulphur and phosphorus. The product of oxidation of arsenic, either phosphorescently or with flame, always contains arsenic oxide, just as some phosphoric oxide and sulphur trioxide are always produced in the parallel cases. The arsenic oxide, which may amount to 1/30th of the whole, seems to be formed directly from arsenic, since arsenious oxide cannot be oxidised under the conditions. The author assumes conversely that arsenic oxide is the sole original product, and this is mainly decomposed into arsenious oxide by a secondary change.

The synthesis of sulphur chloride and arsenic chloride without incandescence is unaccompanied by ionisation. R. J. C.

Formation of Silicon Sulphide in the Desulphurisation of Iron. W. FIELDING (*Trans. Faraday Soc.*, 1909, 5, 110—111).—The object was to find the conditions under which ferrosilicon can react with ferrous sulphide and liberate a sulphide of silicon. The reaction was investigated by heating mixtures of the two compounds in a vacuum at known temperatures. The heating was effected in a crucible in the form of a hollow graphite rod, heated electrically.

With commercial ferrous sulphide the mass fused at about 930°, and a vigorous reaction set in, accompanied by a rise in temperature. With pure ferrous sulphide, no reaction was observed up to about 1300°, so that the reaction noted with the impure compound was probably due to reduction of oxide of iron present by the ferrosilicon.

In all the experiments a yellow sublimate appeared on the walls of the tube at 1500°. This was found to consist of approximately 50% of silicon sulphide (assuming the formula to be SiS_2), the remainder being iron sulphide which had volatilised, silica resulting from the action of moisture in the air on the silicon sulphide, and a small amount of

finely-divided ferric oxide. In different experiments products of variable composition were obtained, and it has not been possible completely to identify the silicon sulphide present in the product.

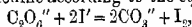
T. S. P.

Thermal Analysis of the System K_2SO_4 -KF. B. KARANDÉEFF (*Centr. Min.*, 1909, 728-733).—On the basis of observations on the rate of cooling of fused mixtures of potassium sulphate and potassium fluoride, a temperature concentration diagram has been constructed. The freezing-point curve consists of three branches corresponding with the two components and with a double salt, KFK_2SO_4 , respectively. The eutectic temperatures, 883° and 788° , correspond respectively with 41 and 83 mols.% of potassium fluoride. The double salt melts at 887° . It is only stable at temperatures above 578° , and on cooling below this, breaks up into its components. Potassium sulphate undergoes a change in crystalline form at 599° .

H. M. D.

Existence of Real Percarbonates and their Differentiation from Carbonates with Hydrogen Peroxide of Crystallisation. E. H. RIESENFELD and B. REINHOLD (*Ber.*, 1909, 42, 4377-4383).—According to the authors, Constan and von Hansen (*Abstr.*, 1897, ii, 550) did not definitely prove that the substance which formed at the anode in the electrolysis of concentrated solutions of potassium carbonate was potassium percarbonate. The substance was never obtained pure, the hydrogen carbonate and water being always present, so that it was possible that it was a hydrogen peroxide additive product of potassium carbonate, since the authors have recently proved the anodic formation of hydrogen peroxide in strong solutions of potassium hydroxide at low temperatures (compare *Abstr.*, 1909, ii, 879).

The authors have now succeeded in preparing a pure potassium percarbonate of the formula $K_4C_2O_6$, and containing neither water nor hydrogen carbonate, so that it could not be an additive product of hydrogen peroxide. It was made by the electrolysis at -30° to -40° of a very strong solution of potassium carbonate, contained in a U-tube. The anode was a platinum wire, the cathode being of platinum foil and surrounded by parchment paper. The current used was 0.5 ampere. After six hours the salt formed at the anode was collected, washed with cold water, alcohol, and ether, and dried, and then proved to have the composition given above. When added to a neutral solution of potassium iodide at the ordinary temperature, it immediately liberates iodine according to the equation:



no oxygen being evolved, whereas hydrogen peroxide reacts very slowly under such conditions. This reaction is characteristic of a real percarbonate, and can be used to distinguish them from additive products of carbonates and hydrogen peroxide. It is found that the percarbonates described by Tanatar (*Abstr.*, 1903, ii, 208), when added to a neutral solution of potassium iodide, cause a brisk evolution of oxygen, and the solution remains colourless. All these compounds

must therefore be classed as additive products of hydrogen peroxide and carbonates. The percarbonates obtained by Wolfenstein and Peltner (Abstr., 1908, ii, 180, 183; 1909, ii, 574) are also doubtful.

It was not found possible to prepare solid percarbonates of lithium, sodium, rubidium, and caesium, although the anolyte reacted towards potassium iodide as if it contained percarbonate. T. S. P.

Reduction of Sodium Sulphate by Carbon. ALBERT COLOS (Compt. rend., 1909, 149, 1076—1078).—When an intimate mixture of sodium sulphate and animal charcoal is heated in an iron pipe, practically no interaction takes place below 950°, but at this temperature the reduction is rapid and uniform, especially if charcoal is used in the proportion required by the equation: $\text{Na}_2\text{SO}_4 + 4\text{C} = \text{Na}_2\text{S} + 4\text{CO}$. With increase of temperature, the rate of action augments rapidly.

T. A. H.

Action of Safety Explosives containing Ammonium Nitrate in the Presence of Carbon, Paper, and Paraffin. H. DAUTHIE (Compt. rend., 1909, 149, 926—928).—Safety explosives containing ammonium nitrate are used in coal mines, and since oxygen is set free in the explosion, it is important to investigate their action on charcoal powder, which would be equivalent to coal dust in the mine, and on paper and paraffin, the latter being used in making the cartridges.

Experiments carried out under conditions very similar to those obtaining in a mine, with an explosive consisting of 90 parts of ammonium nitrate to 7 parts of trinitrotoluene, show that charcoal powder surrounding the cartridges is burnt, and that all the oxygen is used up with the formation of carbon monoxide. The combustion of the paper and paraffin depends on the diameter of the cartridges. When these are 30 mm. in diameter, the combustion is feeble, but when 40 mm. in diameter, it is very marked.

T. S. P.

True Atomic Weights. Stas' Determinations. III. LOUIS DUBREUIL (Bull. Soc. chim., 1909, [iv], 5, 1049—1053, 1053—1055, 1055—1058).—A series of three papers continuing (this vol., ii, 886) the critical revision of Stas' determinations, the cases now considered being (1) silver iodate, (2) silver bromate, (3) silver chlorate.

The apparent atomic weights found for the three cases are: (1) silver 107.9990 and 107.9991, iodine 126.9790 and 126.9991, oxygen 16.0149 and 16.0128, (2) silver 107.9995, bromine 79.9995, and oxygen 16.0061, (3) silver 107.9996, chlorine 35.4996, and oxygen 16.0036.

T. A. H.

So-called Electrolytic Peroxide of Silver. MARGRETE BOSE (Zeitsch. physikal. Chem., 1909, 68, 383—384).—The author's work of the same subject (compare Abstr., 1905, ii, 299) has not been mentioned by Baborovsky and Kuzma (compare Abstr., 1909, ii, 666). G. S.

Silver and Thallium Iridichlorides and Iridochlorides. MARCE DELÉPINE (Compt. rend., 1909, 149, 1072—1074. Compare Abstr. 1908, ii, 702).—The fugitive blue precipitate formed when potassium

iridichloride is added to silver nitrate consists of silver iridichloride, Ag_3IrCl_6 . This when kept, either alone or in presence of excess of silver nitrate, passes into silver iridochloride, Ag_3IrCl_6 , which is yellow, and on treatment with ammonia changes into the greenish-yellow *argentodiammonium iridochloride*, $(\text{Ag}_2\text{NH}_3)_2\text{IrCl}_6$, which loses part of its ammonia on exposure to air and the whole of it on warming (compare Claus, *J. pr. Chem.*, 1847, i, 42, 348).

Thallium iridichloride, Tl_2IrCl_6 , forms small, opaque, greenish-blue cubes, and is more stable than the corresponding silver salt. Boiling hydrochloric acid decomposes it, forming the *iridochloride*, Tl_2IrCl_6 , which crystallises out, on cooling the liquid, in bronze-tinted lamellae. Nitric acid re-converts it into the iridichloride. T. A. II.

The Calcium Silicides and their Absorptive Power for Nitrogen. ADALBERT KOLB (*Zeitsch. anorg. Chem.*, 1909, **64**, 342—367).—By heating together calcium and silicon, two silicides are obtained, according to the component in excess. The products contain 53.6% and 36.68% Si respectively, corresponding approximately with the formulæ $\text{Ca}_5\text{Si}_{10}$ and $\text{Ca}_7\text{Si}_{10}$ (compare Hack-pull, *Abstr.*, 1908, ii, 589; Tamaru, *Abstr.*, 1909, ii, 400). Both silicides are crystalline, evolve hydrogen with acetic acid, and evolve spontaneously inflammable hydrogen with dilute hydrochloric acid. Silicones are obtained with concentrated hydrochloric acid. The first silicide yields an orange or yellow, crystalline silicone, the second yields a silicone containing less silicon.

Both silicides absorb nitrogen actively near 1000° , the first compound being the more energetic. The products have the respective compositions CaSi_2N_3 and $\text{Ca}_{11}\text{Si}_{10}\text{N}_{10}$. Structural formulæ are proposed for the silicides, silicones, and silico-nitrides. C. H. D.

Calcium Ferrites. SIEGFRIED HILPERT and ERNST KOHLMAYER (*Ber.*, 1909, **42**, 4581—4594).—Mixtures of pure ferric oxide and lime are heated in a platinum crucible, protected by an outer crucible of spinel mass, in an electric furnace, of which a hollowed-out carbon rod forms one pole, the other being an outer iron cone, the space between being filled with granulated carbon.

Mixtures containing only small percentages of iron oxide are not completely fusible under these conditions, being on y pasty. The last portion solidifies at 1410° , when they become completely solid. The lime forms well-developed crystals. When the lime falls below 75 mol.%, the primary crystallisation is that of the orthoferrite. The first complete fusion is obtained with 69 mol.% CaO , freezing beginning at 1550° .

Calcium orthoferrite, $3\text{CaO}\cdot\text{Fe}_2\text{O}_3$, melts at 1410° , and disintegrates, like calcium orthosilicate, on further cooling. The next compound, $3\text{CaO}\cdot 2\text{Fe}_2\text{O}_3$, melts at 1450° . At 1220° a reaction occurs in the solid state, the compound formed having a formula near to $5\text{CaO}\cdot 3\text{Fe}_2\text{O}_3$ (compare the aluminate, $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$; Shepherd, Rankin, and Wright, *Abstr.*, 1909, ii, 1015). There is a eutectic point at 1200° and 50 mol.% CaO , and a second maximum at 1400° , corresponding with

the compound $2\text{CaO} \cdot 3\text{Fe}_2\text{O}_3$. Calcium metaferriite, $\text{CaO} \cdot \text{Fe}_2\text{O}_3$, appears to be formed below the eutectic point. The behaviour of mixtures rich in ferric oxide is complicated, partly owing to the escape of oxygen and the formation of crystals of magnetite. Ferric oxide melts at 1565° , and the magnetite oxide at 1527° .

The colour of the mixtures becomes darker with increasing iron. The specific volume curve shows a sharp change of direction at the formula $\text{CaO} \cdot \text{Fe}_2\text{O}_3$, and another, less distinct, near 20 mol. % CaO . The magnetic properties diminish with the proportion of iron, and become insignificant at 67 mol. % CaO . The electrical conductivity is very small throughout, even that of fused ferric oxide being only 10^{-10} that of iron. Solid solutions are not formed, and the low conductivity is unexplained.

The calcium ferrites are much less readily attacked by reagents than the silicates, hence the advantage of their presence in cements exposed to sea-water. The mixtures containing 60–70 mol. % CaO are hydraulic. Calcium ferrites are less easily reducible than ferric oxide.
C. H. D.

Compounds containing Iron Peroxide, FeO_2 . LUDWIG MOESER and H. BORCK (*Ber.*, 1909, 42, 4279–4283. Compare Abstr., 1903, ii, 546).—When a mixture of concentrated solutions of ferric and strontium nitrates (1 mol. : 1–2 mols.) is evaporated to dryness, and the finely-powdered residue heated at a temperature of not more than 600° in a stream of oxygen until oxides of nitrogen are no longer evolved, a compound is obtained which seems to have the formula $\text{SrO} \cdot \text{FeO}_2$. Determination of the proportion of active oxygen to ferric oxide showed that it could not be a compound of strontium peroxide and ferric oxide.

A similar compound was indicated in the residue obtained by heating a mixture of barium hydroxide and ferric hydroxide at 400° in a current of oxygen.

These compounds are black substances, which are stable below 650° , but decompose gradually above that temperature. They are slowly acted on by water with evolution of oxygen. Hydrogen peroxide reacts violently with liberation of oxygen; acids act in a similar manner. Hydrochloric acid gives both chlorine and oxygen; oxalic acid, oxygen and carbon dioxide. Mixtures of air and alcohol or other inflammable vapours, when led over the heated compounds, are oxidised to water and carbon dioxide, and when once the combustion has started, it proceeds of its own accord.

It is possible that a compound of iron peroxide with lithium oxide has been obtained, but it was not found possible to prepare such compounds with other bases.

In an appendix, H. Borck describes a compound of strontium and ferric oxides which is obtained, in a hydrated condition, as a yellowish-brown precipitate by warming a suspension of freshly-precipitated ferric hydroxide in a concentrated solution of strontium hydroxide for some time on the water-bath. On heating, it loses water and becomes brown, and at temperatures above 300° it absorbs oxygen, forming the compound $\text{SrO} \cdot \text{FeO}_2$.
T. S. P.

Hexahydrated Glucinum Sulphate. MARIO LEVI-MALVANO (*Gazzetta*, 1909, 39, ii, 438—440. Compare Abstr., 1906, ii, 165).—The author gives a new example of crystallisation of one salt under the catalytic influence of another dissolved salt.

When prepared in the ordinary way, hexahydrated glucinum sulphate forms a mass of crystals incapable of being measured; but when a solution containing equimolecular proportions of glucinum and potassium sulphates is concentrated on the water-bath and allowed to cool, it deposits large crystals of hexahydrated glucinum sulphate belonging to the cubic system [ZAMBONINI], and melting partly at 78—80° and completely at 95—96°.

T. H. P.

Basic Magnesium Chlorides. WILLIAM O. ROBINSON and W. H. WAGGAMAN (*J. Physical Chem.*, 1909, 13, 673—678).—Solutions containing from 2.36 to 34.22% of magnesium chloride were shaken with small amounts of magnesium oxide for six months at a temperature of 25°. At the end of this time, the residues had become homogeneous, and the solutions constant in composition. From an examination of the diagram on which the solubility data are plotted, the conclusion is drawn that the solid substance in equilibrium with solutions containing less than about 10% of magnesium chloride is an indefinite solid solution, whereas the solid residue in contact with more concentrated solutions is a basic salt of the composition $3\text{MgO} \cdot \text{MgCl}_2 \cdot 10\text{H}_2\text{O}$. Microscopic examination showed that this consists of very small, acicular crystals.

H. M. D.

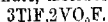
Zinc Amalgams. ERNST COHEN and KATSUJI INOUE (*Chem. Weekblad*, 1909, 6, 921—930. Compare Roozeboom and Byl, Abstr., 1901, ii, 507; Kerp and Böttger, Abstr., 1900, ii, 656; Pushin, Abstr., 1903, ii, 212; Hulett, Abstr., 1900, ii, 543).—The authors have investigated the solubility of zinc in mercury at temperatures between 0° and 100°, and found that it increases. Kerp and Böttger's method gives erroneous results, especially between 20° and 100°. Pushin's results are also incorrect.

A. J. W.

Double Fluorides of Univalent Thallium. FRITZ EPHRAIM and LEONID HEYMANN (*Ber.*, 1909, 42, 4456—4463).—*Thallous manganosomanganic fluoride*, $5\text{TlF} \cdot 2\text{MnF}_3 \cdot \text{MnF}_2$, obtained by precipitating manganous acetate with ammonia and hydrogen peroxide, dissolving the well-washed precipitate in hydrofluoric acid, and adding thallous fluoride, forms claret-coloured prisms, decomposed by water, but soluble in cold concentrated sulphuric acid or in dilute oxalic or tartaric acids to violet solutions, decolorised on heating. Attempts to prepare the manganic compound result in the formation of this salt.

The three *antimony* compounds, $\text{TlF} \cdot \text{SbF}_3$; $\text{TlF} \cdot 2\text{SbF}_3$, and $\text{TlF} \cdot 3\text{SbF}_3$, are all crystalline.

Thallous fluoride and an excess of a solution of vanadium pentoxide in hydrofluoric acid yield minute, insoluble crystals of the salt,



By previously reducing the vanadium solution with sulphur dioxide,

small, green crystals of the salt, $2\text{TlF} \cdot \text{VOF}_5$, are obtained, whilst reduction of the pentoxide with hydrogen, followed by solution in hydrofluoric acid and addition of thallous fluoride, leads to the formation of green crystals of $\text{TlF} \cdot \text{VF}_5 \cdot 2\text{H}_2\text{O}$ or of $2\text{TlF} \cdot \text{VF}_5 \cdot \text{H}_2\text{O}$, according to the proportions taken.

The thallous tantalum compound, $2\text{TlF} \cdot \text{TaF}_5$, forms bright glistening crystals.

Three tungsten compounds, $2\text{TlF} \cdot \text{WO}_2\text{F}_2$, $3\text{TlF} \cdot 2\text{WO}_2\text{F}_2$, and $\text{TlF} \cdot \text{WO}_2\text{F}_2$, are obtained by adding different proportions of thallous fluoride to a solution of tungstic acid in hydrofluoric acid.

C. H. D.

Conditions which Determine the Composition of Electro deposited Alloys. Part I. Copper-Zinc Alloys. SAMUEL FIELD (*Trans. Faraday Soc.*, 1909, 5, 172—194).—To trace the effect of varying conditions on the composition of electro-deposited alloys, the composition of electro-deposited brass, obtained from a cyanide solution under different conditions of (a) composition of solution, (b) strength of solution, (c) temperature, (d) current density, and (e) presence of free cyanide, was determined. The conditions for quantitative deposition from cyanide solutions of the metals separately were first found, and the solutions were then mixed. It was found that, with a solution containing about equal quantities of the two salts in the absence of any notable amount of free cyanide: (a) Copper is the more readily deposited. (b) The percentage of zinc increases with the current density, and also as the amount of zinc compound is increased. (c) Even with a large excess of zinc in the electrolyte, deposits containing a fair proportion of copper are readily obtained. (d) Dilution raises the percentage of zinc, because of the higher *E.M.F.* necessary to maintain the same current density. (e) Rise in temperature increases the proportion of copper deposited. (f) With appreciable amounts of free cyanide the percentage of copper is always high, even with high current density. Free cyanide does not increase the conductivity of the solution to any great extent, but it prevents the formation of insoluble single cyanides at the anode.

Uniform deposition is not maintained in cold stationary solutions, and the insoluble cyanides formed at the anode may completely insulate the plates. With a warm and moving solution, uniform deposits may be obtained without the presence of much free cyanide, the anodes dissolving freely. These cyanide solutions are subject to continual changes of composition which soon prevent the exact repetition of similar conditions. These changes are due to: (1) differing proportions of copper and zinc dissolved at the anodes and precipitated at the cathodes, and (2) to the different amounts of cyanide absorbed or set free by the metals.

The zinc compound used in the above experiments corresponded with the composition $\text{Zn}(\text{CN})_2 \cdot \text{KCN}$, whilst the copper compound had the composition $\text{CuCN} \cdot \text{KCN}$. This latter compound was obtained by saturating a hot solution of Kahlbaum's potassium cuprocyanide, of the composition $3\text{CuCN} \cdot \text{KCN} + 5\text{KCN}$, with freshly precipitated copper carbonate, and then allowing it to crystallise.

T. S. P.

The Corrosion of Iron. J. NEWTON FRIEND (*J. Iron and Steel Inst.*, 1909, Reprint*3—7. Compare Abstr., 1908, ii, 698; *Proc.*, 1909, 25, 90).—A criticism of recent experiments on the rusting of iron. The presence of an acid is necessary to the initiation of rusting.
C. H. D.

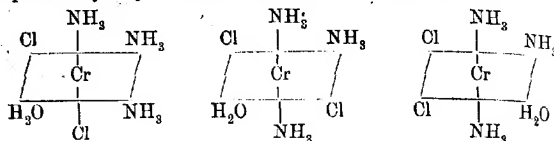
The Action of Air and Steam on Pure Iron. J. NEWTON FRIEND (*J. Iron and Steel Inst.*, 1909, Reprint 2—11. Compare preceding abstract).—At temperatures above 200°, pure iron oxidises in air dried by means of phosphoric oxide. Steam, carefully freed from carbon dioxide, is without action on iron at 100—250°. Slight action begins at 330°, and is rapid at 445°. Traces of air may have been present. Experiments in silica tubes indicate that the temperature at which action begins is near 350°. The action of steam probably takes place in two stages, the steam being first dissociated, and the oxygen thus set free acting on the iron. An estimate is made of the dissociation pressure of iron oxide.
C. H. D.

Reduction of Iron Oxide by Hydrogen and Carbon Monoxide. SIEGFRIED HILPERT (*Ber.*, 1909, 42, 4575—4581).—The temperature at which the reduction of ferric oxide by hydrogen begins, depends on the temperature to which the oxide has been previously heated. A sudden fall in the reducibility of oxide prepared from the hydroxide occurs at 900°, at which point there are indications of a polymorphic change. Oxide prepared from the oxalate only shows this change at 1000°. In both cases the final product behaves like natural hematite, and is only reduced from 330° onwards. It is impossible to obtain a product containing a determined quantity of oxygen by these means, as the reaction takes place unequally in different parts of the mass.

Carbon monoxide is active even at 240°, but the resulting oxide is impure, containing carbon.
C. H. D.

Chromi-aquo-triammines. E. H. RIESENFELD and F. SEEMANN (*Ber.*, 1909, 42, 4222—4232. Compare Abstr., 1906, ii, 760).—If chromtetroxide-triammine is added in small quantities at a time to a cooled dilute solution of hydrochloric acid, a violent reaction takes place, with evolution of oxygen and chlorine and formation of a red solution. Addition of concentrated hydrochloric acid to this solution produces, after a long time, a precipitate of dichloro-aquo-triammine-chromichloride, $\left[\text{Cl}_2\text{Cr} \begin{smallmatrix} \text{OH}_2 \\ (\text{NH}_2)_{2/3} \end{smallmatrix} \right] \text{Cl}$, in the form of reddish-violet, dichroitic crystals, which are soluble in water to a blue solution. If concentrated hydrochloric acid is used instead of the dilute acid, a light green solution is obtained, from which grey, needle-shaped crystals of a second modification of the above chloride separate, which is scarcely soluble in cold water, but dissolves in hot water to a red solution. A third modification is obtained by heating a hydrochloric acid solution of the first chloride for some time at 60°. The solution gradually becomes green in colour, and on evaporation in a desiccator, dark green crystals are obtained, which dissolve in water to a green

solution. Neither of these three chlorides readily loses water, which is therefore probably contained in the complex in all three salts. In all probability they are stereoisomerides:

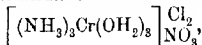


At present it is impossible to say which formula corresponds with which isomeride.

If the aqueous solution of either of the three isomeric chlorides is heated to the boiling point, the colour changes to a violet-red, and on careful evaporation, violet-red crystals of the chlorodiaquatriammine-chromichloride, $\left[(\text{NH}_3)_3\text{Cr}(\text{OH}_2)_2\right]\text{Cl}_2$, are obtained. These crystals are readily soluble in water to a red solution, from which, by the addition of concentrated sulphuric acid and precipitation with alcohol, pale violet, hygroscopic crystals of the chlorodiaquatriamminechromisulphate, $\left[(\text{NH}_3)_3\text{Cr}(\text{OH}_2)_2\right]\text{SO}_4$, are obtained.

Chrometroxide-triammine dissolves in concentrated nitric acid to a red solution, from which rose-red crystals of nitro-diaquatriammine-chrominitrate, $\left[(\text{NH}_3)_3\text{Cr}(\text{OH}_2)_2\right](\text{NO}_3)_2$, separate.

Triaquatriamminechromichloride, $[(\text{NH}_3)_3\text{Cr}(\text{H}_2\text{O})_3]\text{Cl}_3$, is obtained by dissolving chrometroxytriammine in dilute hydrochloric acid and passing hydrogen chloride into the resulting solution. After a time, bright red, needle-shaped crystals of the triaquochloride separate. If the hydrogen chloride is passed in for too long a time, the solution becomes green in colour, and crystals, either of the dichroitic or of the grey monoquochochloride, are obtained. If the aqueous solution of the triaquochochloride is treated with concentrated nitric acid, deep red crystals of the triaquotriammine-chromichloride nitrate,



are obtained.

Each member of the series of the chromi-aquo-triammines, with the exception of the first, $[\text{Cl}_3\text{Cr}(\text{NH}_3)_3]$, has thus been obtained. The separate members are characterised by their different colours, not only as solids, but also in aqueous solution, and it is noteworthy that the colours are exactly analogous to those of the corresponding cobalt compounds, as shown by the following table:

	M = Co.	M = Cr.
$[(\text{NH}_3)_3\text{M}, \text{H}_2\text{O}]$	Bluish-green solution.....	Bluish-green solution.
$[(\text{NH}_3)_3\text{M}, 2\text{H}_2\text{O}]$	Reddish-blue "	Violet-red "
$[(\text{NH}_3)_3\text{M}, 3\text{H}_2\text{O}]$	Purple "	Purple "

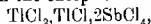
This similarity in colour is all the more remarkable since the ordinary cobalt and chromium salts are so different in colour. The conclusion is therefore drawn that the colour of a salt depends more

its constitution than on the metal which forms part of the cation. Assuming that the atoms in the molecule are bound together by tri-atomic forces, the constitution of the molecule will depend on its iron-content and on the distribution of the electrons. It follows that absorption (of light), electron-content, and the distribution of electrons are all closely connected, a conclusion which has been proved at in quite another way from optical considerations.

T. S. P.

The Isomerism of the Stannic Acids. WERNER MECKLENBURGH *itsch. anorg. Chem.*, 1909, 64, 368—374).—The two modifications of stannic acid are best regarded as colloidal substances, differing in size of their particles, as suggested by van Bemmelen (*Abstr.*, 18, 1160; 1905, ii, 461). The greater adsorptive power and activity of the α -acid indicates that it has the finer structure. The absence of any direct relation of the β -acid to the crystalloid compounds of tin is evidence of its coarser structure. C. H. D.

Double Halogenides of Ter-, Quadri-, and Quinque-valent Antimony. FRITZ EPHRAIM and S. WEINBERG (*Ber.*, 1909, 42, 47—4456).—Derivatives of quadrivalent antimony have a great tendency to decompose into mixtures of compounds of ter- and quinque-valent antimony, with the exception of the thallium salt,



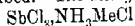
which is stable (Ephraim and Barteczko, *Abstr.*, 1909, ii, 236). The equilibrium $\text{SbCl}_3 + \text{SbCl}_5 \rightleftharpoons 2\text{SbCl}_4$ is greatly dependent on the temperature and on the possibility of ionisation, the addition of phosphoric acid or of salts favouring the tetrachloride.

On adding solid ammonium chloride to a fused mixture of antimony tri- and penta-chlorides, the liquid becomes black, and solidifies on cooling to a violet mass, which slowly loses its colour at the ordinary temperature, ultimately becoming white. The dark metastable salt is not obtained by pouring the hot mixture into chloroform; it then remains for some hours without change.

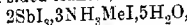
The ammonium compound of antimony tetrabromide, $(\text{NH}_4)_3\text{SbBr}_6$, is prepared by adding the requisite quantity of bromine, followed by ammonium bromide, to a solution of antimony tribromide in concentrated hydrobromic acid, forms black octahedra, stable in air. The free acid was obtained in a state of doubtful purity.

A ferric ammonium antimony chloride, $9\text{NH}_4\text{Cl}, 2\text{FeCl}_3, 3\text{SbCl}_4$, is obtained by mixing the chlorides in concentrated hydrochloric acid, and forms black octahedra. It may be regarded as $3(\text{NH}_4)_2\text{SbCl}_6 + \text{NH}_4\text{Cl}, 2\text{FeCl}_3$.

Compounds of antimony tri- and penta-halogenides with salts of alkylamines are also described. The methylamine compounds,



and $\text{SbCl}_5, \text{NH}_3, \text{MeCl}$, form very large, colourless prisms and microscopic crystals respectively. The bromide, $2\text{SbBr}_3, 3\text{NH}_3, \text{MeBr}, 3\text{H}_2\text{O}$, forms lemon-yellow, six-sided leaflets, and the iodide,

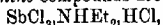


forms yellowish-red leaflets with golden reflex.

The *ethylamine* compounds: $2\text{SbBr}_3 \cdot 3\text{NH}_3 \cdot \text{EtBr}$, a yellow salt containing water; $\text{SbBr}_3 \cdot \text{NH}_3 \cdot \text{EtBr}$, dark red leaflets, and $2\text{SbI}_3 \cdot 3\text{NH}_3 \cdot \text{EtI}$,

are described.

The following *diethylamine* compounds are described:



long, transparent needles; $\text{SbCl}_3 \cdot \text{NHEt}_2 \cdot \text{HCl}$; $\text{SbBr}_3 \cdot \text{NHEt}_2 \cdot \text{HBr}$; $\text{SbBr}_3 \cdot 2\text{NHEt}_2 \cdot \text{HBr}$, black crystals, violet in thin fragments; and $\text{SbBr}_3 \cdot \text{NHEt}_2 \cdot \text{HBr}$, garnet-red, rectangular crystals. C. H. D.

Effect of Ferric and Cupric Salt Solutions on Gold. W. J. McCaughey (*J. Amer. Chem. Soc.*, 1909, 31, 1261—1270).—In the analysis of gold bullion containing a large proportion of tin, it was found that the gold could be most conveniently separated by precipitation with ferrous sulphate. The precipitate, however, still contained tin, and if sufficient hydrochloric acid was present to keep all the tin in solution, the gold was not completely precipitated.

Preliminary experiments having shown that gold is soluble in solutions of both ferric and stannic salts in presence of hydrochloric acid, an investigation was carried out to ascertain the effect of the concentration of the salt and acid and the presence of ferrous sulphate on the solubility. The solvent action of cupric chloride was also studied. The experiments were conducted at $38-43^\circ$ and at $98-100^\circ$. The results are tabulated and plotted as curves.

It has been found that gold is soluble in solutions of iron alum and cupric chloride containing hydrochloric acid, the solubility increasing with the concentration of the acid or salt. An increase in the concentration of the acid has a greater effect on the solubility than an increase in the concentration of the salt, and particularly in the case of the copper salt. The rate of solubility in the presence of iron alum is eleven times greater at $98-100^\circ$ than at $38-43^\circ$, and in the presence of cupric chloride is 32 times greater at the higher temperature. By doubling the concentration of the acid, the solvent action of cupric chloride solution is increased seven times at $38-43^\circ$ and five times at $98-100^\circ$. Iron alum is capable of dissolving gold even in presence of a ferrous salt, but the solvent action decreases as the concentration of the ferrous salt increases. In the precipitation of gold by ferrous sulphate, it is therefore advisable to use considerable excess of the reagent, and to allow the solution to cool before filtering it, since the solvent action of ferric salts is much greater at the higher temperatures. The solubility of gold in solutions of ferric salts gradually decreases with time and approaches a limit, but in the case of cupric chloride the amount of gold dissolved is directly proportional to the time. E. G.

Gold Hydrosols. CARL THOMÆ (*J. pr. Chim.*, 1909, [ii], 80, 518—520).—Zsigmondy's red-gold hydrosol, which can be kept for a year, is prepared with water distilled repeatedly through a silver condenser. However, a hydrosol, which is tenable for four months, can be obtained with ordinary distilled water as follows. The water, 120 c.c., is brought to the boil in a Jena flask, and 2.5 c.c. of gold

chloride solution (1 gram of crystallised salt : 167) and 3.2 c.c. of potassium carbonate (2.5 : 100) are added successively. Whilst the water is boiling vigorously and the flask is being violently shaken, 5.0 c.c. of formaldehyde solution (3 grams of commercial approximately 36% formalin : 100) are added drop by drop. If the first drop causes a separation of gold, the addition is stopped, and the boiling is continued until the gold has disappeared. Gold should not separate until many drops of the formaldehyde have been added; then the formation of a slight gold mirror is immaterial. The liquid is blue at first, and finally dark red. It is decanted into another flask. The formation of a filminess or turbidity indicates that the reducing agent has been added too quickly, or in too large quantities. C. S.

Magnesium Aurides. G. G. URZOFF (*Zeitsch. anorg. Chem.*, 1909, **64**, 375—396. Compare Vogel, Abstr., 1909, ii, 896).—Alloys of gold and magnesium are best prepared by heating the components in the proportions required to form the compound AuMg in a graphite crucible enclosed in an iron cylinder with screw cap. Combination takes place readily at 700°, and the compound may be fused quietly with further quantities of gold or magnesium under a layer of alkali chloride.

Four compounds are indicated on the freezing-point curve: AuMg, with a maximum at 1150°; AuMg₂, with a maximum at 788°; Au₂Mg₃, at a break in the curve at 798°, and AuMg₃, with a third maximum at 818°. Gold forms solid solutions with nearly 30 atomic % Mg, and the compound AuMg forms solid solutions ranging from 42 to 66 atomic % Au. The compound Au₂Mg₃ undergoes a transformation at 721°.

Alloys rich in gold may be etched with hydrochloric acid and bromine; those containing little gold are etched sufficiently by polishing while wet. The microscopical examination confirms the indications of the cooling curves. C. H. D.

Atomic Weight of Platinum. EBENEZER H. ARCHIBALD (*Proc. Roy. Soc. Edin.*, 1909, **29**, 721—747).—From a consideration of earlier determinations, the author draws the conclusion that the platinum salts analysed must have contained appreciable amounts of impurities, for very divergent results are obtained when the weight of original salt is used in the calculation of the atomic weight. To obtain pure platinum the metal was precipitated in the form of ammonium platinichloride, the precipitate being thoroughly washed and dried and then reduced in a current of pure hydrogen. After removal of ammonium chloride, the platinum-black was boiled with successive portions of concentrated hydrochloric acid to dissolve out traces of iron. The platinum was then redissolved, and the above processes repeated several times. After three operations all indications of iridium had disappeared. To avoid the difficulty of removing the last traces of nitric acid from a solution prepared by dissolving platinum in aqua regia, the metal was brought into solution by making it the anode in an electrolytic cell containing hydrochloric or hydrobromic acid. From such solutions the potassium and ammonium salts of chloro- and bromo-platinic acid

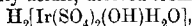
were prepared. With these four salts, four series of determinations were made by reduction in a current of pure dry hydrogen. Before reduction the potassium salts were heated at 400° , and the ammonium salts at 175° , for the purpose of expelling absorbed and occluded moisture. After reduction, the platinum metal, the halogen salt, and the halogen acid given off were estimated. These measurements give several ratios from which the atomic weight of platinum can be deduced. Rejecting those in which the weight of original salt is concerned, twelve values are obtained for the atomic weight, the lowest of which is 195.21, and the highest, 195.24. The mean value adopted is 195.23. ($O = 16$.)

Incidentally, it is shown that the same results are obtained for the weight of reduced platinum, whether this is heated and cooled in hydrogen and weighed at atmospheric pressure, or heated, cooled, and weighed in a vacuum.

H. M. D.

Metallic Iridium Disulphates. MARCEL DELÉPINE (*Compt. rend.*, 1909, 149, 785—788; *Bull. Soc. chim.*, 1909, [iv], 5, 1084—1088, 1126—1133. Compare Abstr., 1909, ii, 408).—The action of sulphuric acid on potassium iridochloride gives a blue solution which does not contain a salt of the same type as the ammonium iridium disulphates already described. The ammonium in the latter can, however, be wholly or partly replaced by potassium, sodium, thallium, and barium.

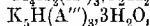
The iridium disulphates fall into two series, namely, the green salts, which are generally acidic, derived from the acid,



designated H_3A'' , and the reddish-brown salts, which are basic, derived from the acid, $H_3[Ir(SO_4)_2(OH)_2]$, designated H_3A''' . These tautomeric acids are easily converted into one another by addition of excess of base and acid respectively.

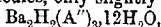
The following basic salts are described: $K_7H_2(A''')_3 \cdot 6H_2O$, crystallising in needles varying in colour from old rose to blackish-brown, according to thickness. This salt is prepared by pouring a cold solution of $NH_4 \cdot H_3(A'')_2$ into excess of potassium carbonate solution. $Na_7H_2(A''')_3 \cdot 6H_2O$ and $9H_2O$, reddish-brown clusters of needles or rectangular plates, is obtained by precipitation with alcohol. $Tl_{21}(NH_4)_4 \cdot H_3(A''')_{12}$ and $Tl_7H_3(A''')_2 \cdot 4\frac{1}{2}H_2O$, dark brown crystals, are very slightly soluble. $Ba_7H_4(A''')_6 \cdot Aq$ is a greenish-brown, amorphous precipitate, turning pure green on exposure to air and slowly depositing barium sulphate.

The salts of the acid H_3A'' are all soluble in water, but less soluble in presence of alcohol, ether, or another salt of the same metal. The following were prepared by a variety of methods from the corresponding ammonium salts: $K_2NH_4H_3(A'')_3 \cdot 3H_2O$, green to black needles according to size. $K_3H_3(A'')_3 \cdot 1\frac{1}{2}H_2O$, needles.

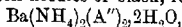


hexagonal or octahedral crystals. $K_3(A'')_3 \cdot H_2O$, opaque, square crystals, very dark green; their solution is alkaline, and of an impure green colour. $K_2H_4(A'')_3 \cdot 6H_2O$, tetrahedra, stable only in strong acids. $Na_3 \cdot NH_4 \cdot H_3(A'')_3 \cdot 18H_2O$, very soluble black crystals, almost

rectangular. $\text{Ti}_7(\text{NH}_4)_2\text{H}_2(\text{A}'')_6$ to $\text{Ti}_7\text{H}_5(\text{A}'')_6, 6\text{H}_2\text{O}$, a mixture consisting of small, green needles, only slightly soluble in water.



crystallising in long, green needles or black, rectangular crystals.



small, opaque, black tetrahedra.

R. J. C.

Osmium. ALEXANDER GUTHRIE and K. MAISCH (*Ber.*, 1909, 42, 4239—4243).—In preparation for a revision of the atomic weight of osmium, the authors have submitted the osmichlorides to a systematic investigation. Sodium osmichloride was first prepared by heating a mixture of sodium chloride and osmium in a current of chlorine. If the osmium is in the form of granules, the reaction takes place extremely slowly, but when the metal is in a finely divided condition, the reaction is complete in about half-an-hour at a red heat. The sintered mass which is thus obtained was dissolved in cold dilute hydrochloric acid, the solution filtered, and the filtrate saturated with hydrogen chloride to precipitate any sodium chloride present. After further filtration, the sodium osmichloride was obtained by careful evaporation of the filtrate; this salt could not, however, be prepared in a quite pure condition. It was therefore used to prepare the osmichlorides of ammonium, potassium, rubidium, and caesium by double decomposition with the chlorides of these metals. All these compounds are much less soluble than sodium osmichloride, and, after recrystallisation from dilute hydrochloric acid, they are obtained as dark-coloured, well-defined, octahedral crystals which are stable in dry air; on being powdered they each give a bright red powder. They are soluble in cold water, but the solutions decompose on exposure to the air, after a time depositing a black powder. They are easily soluble in dilute hydrochloric acid, giving stable solutions.

With the exception of the sodium salt, all these compounds are anhydrous.

T. S. P.

Mineralogical Chemistry.

The Need for a Systematic Study of Optically Active Petroleum. MICHAEL RAKUSIN (*Ber.*, 1909, 42, 4675—4678. Compare Abstr., 1909, ii, 246, 490, 586).—Mainly polemical. A reply to Ubbelohde (Abstr., 1909, ii, 899).

J. J. S.

Selenium in Altai Minerals. P. P. PILIPENKO (*Bull. Acad. Sci. St. Pétersbourg*, 1909, 1113—1115).—Two samples of galena from the Altai mountains were found to have the following compositions:

	Se.	S.	Pb.	Cu.	Fe.	SiO ₂ .	Total.
I.	1.17	12.60	82.28	1.28	0.48	2.02	99.83
II.	1.23	13.40	83.72	0.34	0.47	0.48	99.64

The mean composition, given by two analyses, of a sample of grey copper from a mine in the Altai district is as follows :

Se.	S.	Sb.	As.	Cu.	Ag.	Fe.	Co.	Zn.	SiO ₂ .	Total.
0.13	24.48	25.71	1.68	39.16	trace	2.00	0.23	4.87	0.95	99.21

A number of other Altai minerals, and also the sulphide compounds of the Mineralogical Museum of Tomsk University, were examined, but the above specimens were the only ones containing selenium.

T. H. P.

A Pitchblende probably occurring in New South Wales. T. H. Laby (*J. Roy. Soc. New South Wales*, 1909, 43, 28—33).—The author has examined a pitchblende which was probably obtained from the New England district of New South Wales, although the exact locality is unknown. Analysis of the mineral gave :

UO ₂ .	UO ₂ .	PbO.	Mn ₂ O ₄ .	Fe ₂ O ₃ .	CaO.	Bi ₂ O ₃ .	CuO.	As ₂ O ₃ .	MgO.	SiO ₂ .	Insol. H ₂ O.
69.0	8.8	6.0	4.2	2.7	3.7	0.4	0.1	trace	trace	0.1	2.4 0.69

The powdered mineral has D²⁵ 7.65. Its radioactivity is 4.4 times that which would result from the amount of uranium present. The absence of rare earths, the presence of CuO, Br₂O₃, and As₂O₃, the large proportion of UO₂, and the massive and non-crystalline form of the mineral indicate that it is probably a secondary pitchblende.

H. M. D.

Rhodizite in the Pegmatites of Madagascar. ALFRED Lacroix (*Compt. rend.*, 1909, 149, 896—899).—The author has recently noted the presence of the two borates, danburite (Abstr., 1909, ii, 812) and hambergite (BO₃Gl₂·OH), in the pegmatites of Madagascar. Tetrahedral crystals, 1½ cm. across, of rhodizite have now been found embedded in the gem spodumene of a pegmatite-vein at Antandrokomby; the pegmatite is composed also of quartz, microcline, albite, red and yellow tourmaline, and a tantalocolumbate, probably identical with microlite. The rhodizite crystals are whitish-yellow with a tinge of green; they are pseudo-cubic, with optical anomalies similar to those of boracite. Mean refractive index (Na) 1.63, H 8, D 3.305. Analysis by F. Pisani gave :

B ₂ O ₃ .	Al ₂ O ₃ .	GlO.	Li ₂ O.	K ₂ O (+Cs ₂ O).	Na ₂ O.	SiO ₂ .	Loss on ignition.	Total.
40.60	30.50	10.10	7.30	5.90	3.30	1.86	0.45	99.51

Deducting silica and the corresponding amount of alumina and lithia, present as admixed spodumene, this analysis gives the formula 6B₂O₃·3Al₂O₃·4GlO·4(Li,K,Na,H)₂O.

Damour's analysis (1882), made on only a small quantity of the rare and minute crystals of the Uralian rhodizite, showed no glucinum or lithium; it is remarked, however, that his percentage of alumina (41.40) is equal to the sum of the alumina and glucina in the above analysis, and a qualitative test now made on a Uralian crystal showed the presence of lithia.

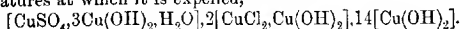
L. J. S.

Pucherite from West Australia. E. GRIFFITHS (*J. Roy. Soc. New South Wales*, 1908, 42, 251—252).—The concentrates from an oxidised quartz reef at Niagara, 115 miles north of Kalgoorlie, W. A., have been found to contain pucherite in the form of approximately cubical, crystalline grains, chrome-yellow in colour, brittle, and with a resinous lustre, D 5.7. Analysis gave the following results: Bi_2O_3 73.77%, V_2O_5 (including trace of P_2O_5) 25.31%, Fe_2O_3 0.36%, residue insoluble in hydrochloric acid 0.81%. H. M. D.

Connellite and Chalcophyllite from Bisbee, Arizona. CHARLES PALACHE and H. E. MERWIN (*Amer. J. Sci.*, 1909, [iv], 28, 537—540).—A single small specimen from the Calumet and Arizona mine at Bisbee consists of groups of radiating needles of dark blue connellite together with cuprite, melanochalcite, and chalcophyllite. The connellite prisms are terminated by the unit pyramid, and measurements gave $a:c = 1:1.185$; refractive indices $\omega 1.724$, $\epsilon 1.746$; D 3.396. Analysis (by Merwin) on 0.73 gram gave:

SO_2 .	Cl.	CuO.	H_2O ($<220^\circ$).	H_2O ($220-260^\circ$).	H_2O ($260-360^\circ$).	H_2O ($>360^\circ$).	Total (less O for Cl).
3.43	6.37	75.96	0.25	12.06	2.10	1.66	100.41

This differs somewhat from the only analysis previously made of connellite (Penfield, 1890, on only 0.074 gram), and corresponds with $\text{Cu}_{22}\text{Cl}_2\text{SO}_{23}\cdot 20\text{H}_2\text{O}$, or, distributing the water in accordance with the temperatures at which it is expelled,



The crystals of chalcophyllite present many points of resemblance to spangolite, but they were found to contain copper, aluminium, and arsenic. Measurements gave $a:c = 1:2.671$. L. J. S.

The Earths of Euxenite. OTTO HAUSER and FRITZ WIRTH (*Ber.*, 1909, 42, 4443—4447).—Specimens of euxenite from (I) Eitland, (II) Arendal, (III) Sietersdal, (IV) South Carolina, gave the following analyses:

	Ca_2O_2	Ta_2O_5	TiO_2	SnO_2	WO_3	UO_2	ThO_2	Y_2O_3
I.	29.00	1.01	24.43	0.11	trace	5.64	4.60	27.32
II.	30.21	—	26.45	—	—	5.28	3.20	28.47
III.	20.72	—	31.45	0.13	0.09	5.19	3.80	25.42
IV.	28.20	9.35	17.45	0.07	0.11	7.91	2.04	22.01

	$\text{Ce}(\text{Sa}, \text{Di})_2\text{O}_3$	Al_2O_3	FeO	CaO	MgO	PbO	Loss on ignition.	Total.
I.	2.45	trace	1.37	0.85	0.08	0.43	2.87	100.16
II.	2.05	—	1.89	0.87	—	—	2.01	100.64
III.	2.58	—	4.94	0.66	0.14	0.46	3.83	99.76
IV.	6.93	—	2.04	—	—	0.96	2.21	99.28

Of these, I and II are typical euxenites, III is to be regarded rather as a polycrase, whilst IV differs from both in containing an unusually large quantity of tantalum acid and a relatively small quantity of titanic acid.

Of the yttrium group, yttrium is always in excess. With increasing

titanium, holmium and dysprosium increase relatively to neo-erbium. The components of ytterbium are abundant, and scandium occurs, especially in polycrase, where it attains 0.06%. Samarium and praseodymium are absent from normal euxenites, but samarium is found with increasing tantallic acid. Zirconium could not be detected in any of the specimens.

C. H. D.

Bertrandite from Altai. P. P. PILIPENKO (*Bull. Acad. Sci. St. Pétersbourg*, 1909, 1116—1118).—The author describes crystals of bertrandite occurring in the aquamarine deposits of the Altai mountains. The crystals have a glassy lustre, are mostly colourless and transparent, and form either long plates or prisms elongated along the z axis; D^{20} 2.603, hardness 6. Their composition is as follows:

SiO_2	Al_2O_3	Fe_2O_3	CaO	GIO	H_2O	Total
50.12	trace	trace	trace	40.67	8.87	99.56

This bertrandite is formed as a result of the weathering of beryl, and itself undergoes further change.

T. H. P.

Sardinian Minerals: Species from the Province of Sassari. AURELIO SERRA (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 348—350. Compare Abstr., 1909, ii, 492, 494).—A sample of heulandite, in which the angle $110:110$ had a value of about 47° , was found to have the composition:

SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	H_2O	Total
61.12	15.61	6.04	0.53	2.23	0.94	14.32	100.79

corresponding with the formula $(\text{Ca}, \text{Mg}, \text{Na}, \text{K})\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 5\text{H}_2\text{O}$. As typical heulandite contains SiO_2 , 59.2; Al_2O_3 , 16.8; CaO , 9.2, and H_2O , 14.8%, the abnormal value of the angle $110:110$ depends on the variations in chemical composition.

A sample of mesolite from "Su Marralzu" gave on analysis:

SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	H_2O	Total
50.85	21.95	12.02	0.08	1.72	trace	14.61	101.23

and a sample of Smithsonite from the Sos Enattos (Lula) mines:

ZnO	FeO	CaO	CO_2	Total
62.60	1.22	1.53	35.77	101.12

T. H. P.

Lujaurites from Pilandsberg (Transvaal). H. A. BROUWER (*Compt. rend.*, 1909, 149, 1006—1008).—The analyses of two different kinds of lujaurite from the Transvaal are given. The one (I) is very similar to lujaurite from the Kola peninsula (Lapland), whilst the other (II) is rich in ægyrine and endialyte:

	SiO_2	TiO_2	ZrO_2	Al_2O_3	Fe_2O_3	FeO	MnO	CaO
I.	52.35	0.59	0.89	14.11	7.98	2.17	0.62	4.65
II.	51.35	2.75	0.54	11.45	9.40	2.41	1.25	3.27

	MgO	K_2O	Na_2O	CO_2	H_2O	Total
I.	0.86	2.78	9.30	1.50	3.20	100.30
II.	0.54	2.52	10.80	—	3.20	99.48

As compared with other lujaurites, these are rich in lime, because of the presence of calcite. The decrease in Al_2O_3 and increase of Fe_2O_3 in (II) as compared with (I) is due to the former being rich in agyrine.

T. S. P.

Rhönite from Puy de Barneire at Saint-Sandoux. ALFRED LACROIX (*Bull. Soc. franç. Min.*, 1909, 32, 325—331. Compare Abstr., 1907, ii, 972; 1909, ii, 587).—Large, black crystals with a brilliant greasy to metallic lustre are present in a doleritic nephelinite at this locality. Under the microscope these resemble the rhönite of the Rhön mountains, but owing to the depth of colour and intense pleochroism, their optical characters could not be completely determined; D 3.56. The following analysis by F. Pisani gives the formula: $(\text{Na}, \text{K}, \text{H})_2\text{Ca}_8(\text{Fe}, \text{Mg})_{15}(\text{Al}, \text{Fe})_{16}(\text{Si}, \text{Ti})_{21}\text{O}_{90}$.

SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	H_2O	Total
30.90	8.04	17.65	6.80	15.20	9.03	12.20	0.76	0.61	0.20	100.64

L. J. S.

Deposits from the Mineral Water of the Rohitsch Springs, Styria. HANS LEITMEIER (*Zeitsch. Kryst. Min.*, 1909, 47, 101—123).

—The waters of the springs at Rohitsch contain carbon dioxide with considerable amounts of magnesium carbonate, sodium sulphate and carbonate, and much less calcium carbonate, etc. Fine crystal groups of aragonite have been deposited naturally by these waters, and quartz crystals, $\frac{1}{2}$ cm. in length, are also noted. The mineral water was allowed to evaporate slowly in the air at temperatures of 2° , 13° , and 20° . At the two higher temperatures, acicular, rhombic, crystals of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ (anal. I), identical with the mineral nesquehonite, were formed after some days; and later there was a deposit of indistinct crystals of aragonite. When, however, the evaporation took place at the lower temperature (2°) there was, after one-and-a-half months, a deposit of large, tabular, monoclinic crystals of the pentahydrate, $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$ (anal. II). This salt is not formed at temperatures above 6° . It commences to lose water in the air at 20° , and at 60° , four-fifths is lost; at 100° the loss is 44.68%, and at 300° , 51.69%. These crystals have the same geometrical constants

$$[a:b:c = 1.6079:1:0.9524; \beta = 78^\circ 36']$$

as the mineral lansfordite ($3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 21\text{H}_2\text{O}$), and as the supposed tetrahydrate of magnesium carbonate described by Marnignac. These three thus appear to be identical, the analyses of the last two having been made on partly dehydrated material:

	MgO	CaO	CO_2	H_2O	Total	Sp. gr
I.	23.52	—	[31.09]	40.03	99.64	1.354
II.	23.18	trace	25.21	51.69	100.08	1.688

L. J. S.

Physiological Chemistry.

Asphyxia in the Spinal Animal. R. KATA and ERNEST H. STARLING (*J. Physiol.*, 1909, 39, 346—353).—In asphyxia the increased tension of carbon dioxide in the blood excites the brain centres, including those in the bulb; this produces exaggerated attempts to breathe, and a rise of arterial pressure, but no injurious action on the heart. The convulsions which follow are due to excitation of the spinal centres by lack of oxygen, and the heart failure, which leads to a fall of pressure, is also due to the same cause.

W. D. H.

Supposed Presence of Carbon Monoxide in Normal Blood and in the Blood of Animals Anaesthetised with Chloroform. GEORGE A. BUCKMASTER and JOHN A. GARDNER (*Proc. Roy. Soc.*, 1909, B, 81, 515—528).—For detecting carbon monoxide, the authors use the spectroscopic test and the admittedly delicate method of Haldane. Carbon monoxide is not a normal constituent of blood-gases. Chloroform is not decomposed in the blood with the formation of carbon monoxide. Chloroform vapour contained in the blood-gases of anaesthetised animals yields carbon monoxide when these gases are passed over potash. The small quantities of iodine found in Desgrez and Niclaux's experiments, in which the normal blood-gases are passed over iodine pentoxide at 150°, are probably due to the decomposition of this substance at this temperature.

G. S. W.

Comparison of the Haemoglobin of certain Molluscs with that of Vertebrates. RAFFAELE PALADINO (*Biochem. Zeitsch.*, 1909, 22, 495—505).—The haemoglobin from various molluscs was compared with that obtained from *Scyllium* and the dog. It did not differ essentially from these, although certain minor differences were observed; the mollusc blood, for example, is more readily changed by 10% acetic acid, and less readily by 10% sodium hydroxide solution; it is also more difficult to obtain in crystalline form.

S. B. S.

Effect of Temperature on the Dissociation Curve of Blood. JOSEPH BARCKROFT and W. O. R. KING (*J. Physiol.*, 1909, 39, 374—384).—Dissociation curves of undialysed haemoglobin solution in water are given at different temperatures in the presence and absence of carbon dioxide; in a solution of potassium chloride, the presence of carbon dioxide is relatively more powerful in the reduction of haemoglobin than in the removal of oxygen. In low forms of animal life, in which haemoglobin is retained in store in muscles or nervous tissue, the oxygen can be withdrawn in case of need, for instance, in partial asphyxia or great activity; a favourable condition for the ready withdrawal of oxygen would be rise of temperature or rise of carbon dioxide tension. The influence of temperature is evident also in the blood. In muscular exercise, with its accompanying rise of tempera-

ture, in fever, and in inflammation, the organism, or part of it, requires oxygen at a more rapid rate than usual; the rise of body-temperature enables the blood to meet this demand, and is, in fact, the counterpart of vascular dilatation.

W. D. H.

Hæmolysis. OSCAR GROS (*Arch. exp. Path. Pharm.*, 1909, 62, 1—38).—Hæmolysis is due to two factors: (1) the death of the corpuscles; (2) to physico-chemical changes which lead to the passage of hæmoglobin out of them. The second factor can be best studied if the changes occur rapidly, as when caused by ammonia. The velocity of the change is then proportional to the concentration of the ammonia, and inversely proportional to the concentration of the blood. Various salts were studied in the same way at different temperatures. Various ions favour hæmolysis at 47.5° in the following order: $\text{Na} < \text{Mg} < \text{K} < \text{Ca}$; $\text{Cl} < \text{SO}_4$; and at 50°, $\text{Mg} < \text{Na} < \text{K} < \text{Ca}$; $\text{Cl} < \text{SO}_4$. The inhibitory action of serum on hæmolysis is not destroyed by heating to 65°.

W. D. H.

The Disintegration and Life of Blood-platelets. H. DEETJEN (*Zeitsch. physiol. Chem.*, 1909, 63, 1—26).—Blood-platelets from human blood can be isolated by collecting the blood between the object glass and cover slip, and washing with physiological saline. In this way the other elements can be removed; the platelets alone remain sticking to the glass. They rapidly disintegrate under ordinary conditions, but remain, however, intact if quartz is used instead of glass, and the saline solution is perfectly neutral. In the presence of minute traces of alkali ($C_{\text{OH}} = 10^{-5}$) and of somewhat larger quantities of acid ($C_{\text{H}} = 2 \cdot 10^{-4}$) they disintegrate. The action of the hydroxyl ions is indirect; they either influence a ferment or cause the liberation of a ferment which causes the disintegration of the platelets. This statement is made in consequence of the fact that even in the presence of alkali the platelets can under certain conditions remain intact. Thus, they are protected from disintegration by the presence of hirudin, manganese salts, Witte's peptone, and peroxides. From the investigations with hirudin, the conclusion is drawn that the platelets themselves secrete an enzyme, which leads finally to their destruction. The platelets after treatment with hirudin are not disintegrated by alkali, although they are by plasma. The destroying ferment is not identical with the blood-clotting ferment, although it is possibly with the pro-ferment. Manganese salts do not entirely inhibit the disintegration, but only retard it; on the other hand, they inhibit blood-clottings, owing perhaps to action on the pro-ferment. Witte's peptone paralyses the platelets, and thus inhibits the secretion of the ferment. Peroxides entirely inhibit the disintegration of the isolated ferments. The explanation of this fact is not obvious. By means of the peroxide method, the action of the living platelets can be demonstrated. The presence of a nucleus, nuclear membrane, and amœboid movement can then be shown. The disintegration of the platelets after removal from the blood-vessels is due to the evolution of carbon dioxide and the increased concentration of the

hydroxyl ions. The platelets from other animals are not all identical with those from man; those from the ape are very similar.

S. B. S.

Spectro-photometry of Blood. EUGEN LETSCHE (*Zeitsch. physiol. Chem.*, 1909, 63, 313—314).—Remarks on the usefulness of Hüfner's spectro-photometer. In spite of its faults, it gives good results in accustomed hands.

W. D. H.

Influence of Stereochemical Configuration on Certain Physico-chemical Properties of Organic Colloids. GIUSEPPE BUGLIA and L. KARCZAG (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 374—380).—The authors have determined the influence of *d*, *l*, *i*, and α -tartaric acids in various concentrations on the time of coagulation by heating of normal blood-serum and of blood-serum dialysed until it has become neutral.

All these acids have a marked influence on the coagulation, at first accelerating it, and subsequently retarding, and even absolutely preventing, it. *i*-Tartaric acid, which is dissociated to a less extent than the other acids, also produces less acceleration of the coagulation, and renders the serum non-coagulable in lower concentrations than with the active and racemic acids. With these three acids, which are approximately equally dissociated, the influences on the coagulation are about the same.

T. H. P.

The Laws of Digestion and Absorption. SVANTE ARRHENIUS (*Zeitsch. physiol. Chem.*, 1909, 63, 323—377).—A mathematical discussion of the laws relating to the velocity, etc., of digestive processes. The rule of the square root appears to play a dominating part. London's work on the subject is on the whole corroborated.

W. D. H.

The Enzymes concerned in Nuclein Metabolism in Human Organs. ALFRED SCHITTENHELM. **The Fate of Nucleic Acid contained in the Food of Normal Men.** FRANZ FRANK and ALFRED SCHITTENHELM. **The Occurrence and Importance of Allantoin in Human Urine.** ALFRED SCHITTENHELM and KARL WIENER. **The Enzymes Concerned in Nuclein Metabolism in Lupin Seedlings.** ALFRED SCHITTENHELM (*Zeitsch. physiol. Chem.*, 1909, 63, 248—268, 269—282, 283—288, 289).—The capacity of the human liver and other organs to form uric acid is undoubted, and can be readily demonstrated in extracts by their action on guanine. Commenting on W. Jones' statement regarding the absence of adenase in human organs, it is pointed out that unquestionably adenine disappears during life, the urine containing only traces after abundant ingestion of that substance when sweetbread is taken as food. It is therefore doubtful whether the action of extracts is a true index of actual metabolism; if an extract gives a positive result, it is no doubt of the same nature as that occurring during life; but if a negative result occurs, that does not necessarily mean that a positive result will not occur during actual metabolism in the living organ. It is of course true, again, that extracts of human organs contain no uricolytic principle.

enzyme, that is to say, destruction of uric acid does not occur post-mortem; it is unscientific to conclude from this, that uricolysis does not occur during life.

Both in animals and men, nucleic acid given in the food is completely absorbed and undergoes metabolism, and the end-products are excreted during the same day. This comes out quite clearly by a study of nitrogen and phosphorus excretion. The proportion between the different end-products varies in different animals; in man, the main one is urea, the uric acid formed is small in amount, and the purine bases of the urine are minimal. The uric acid formed is doubtless again largely destroyed, and the nitrogen finally is contained in urea.

The meaning of allantoin in the urine is far from clear; if uric acid precursors are administered, the amount of allantoin does not increase in the urine. If allantoin is given by the mouth or subcutaneously, about 30% is recoverable in the urine. It cannot therefore be an important end-product of uric acid catabolism.

The expressed juice, or aqueous extracts of lupin seedlings, contain an amidase which converts guanine into xanthine. W. D. H.

The Elimination of Total Nitrogen, Urea, and Ammonia following the Administration of Amino-acids, Glycylglycine, and Glycylglycine Anhydride. PHOEBUS A. LEVENE and G. M. MEYER (*Amer. J. Physiol.*, 1909, 25, 214—230).—The results of these metabolism experiments on dogs are given with full detail; the extra nitrogen administered is usually excreted within twenty-four hours, but this rate varies, and the proportion of urea, ammonia, etc., also varies in different cases. It is specially rapid after the ingestion of amino-acids. W. D. II.

The Influence of Removal of Segments of the Gastro-intestinal Tract on the Character of Protein Metabolism. ISAAC LEVIN, D. D. MANSON, and PHOEBUS A. LEVENE (*Amer. J. Physiol.*, 1909, 25, 231—253).—After excision of portions of the alimentary canal, an unexpected acceleration in the absorption and elimination of nitrogen is the most noteworthy result. W. D. H.

The Influence of Certain Mercury Compounds on Metabolism. GUIDO IZAR (*Biochem. Zeitsch.*, 1909, 22, 371—393).—Mercury when introduced directly into the circulation, either in form of a hydrosol or of salts, markedly stimulates the nitrogenous metabolism, and the amount of nitrogen in the urine is considerably increased. Larger doses, however, of sublimate, calomel, hygro, and mercuric thiosulphate are necessary to produce the same effect as a given dose of the hydrosol. There is no difference between the actions of stabilised and non-stabilised colloids. The increase of urea and uric acid in the urine runs parallel with the increase in total nitrogen. S. B. S.

[The Permeability of Cells for Dyes.] W. RUHLAND (*Biochem. Zeitsch.*, 1909, 22, 409—410).—The author objects to the attempted explanation of Hüber (Abstr., 1909, ii, 912) of the reason why wool-

violet-S and other dyes do not behave in accordance with the Overton lipid theory. S. B. S.

Nucleo-protein in the Yolk Platelets of the Frog's Egg; and the Black Pigment. J. E. McCLENDON (*Amer. J. Physiol.*, 1909, 25, 195—198).—The nucleo-protein investigated is probably more properly to be considered a lecitho-protein or vitellin-like substance. It is termed *batrachiolin*; it contains P 1.2%, S 1.32%, and N 15.14%. Analyses are also given of the black pigment which appears to belong to the melanins, but it was not satisfactorily freed from impurities. W. D. H.

The Catalase of Echinoderm Eggs before and after Fertilisation. ELIAS P. LYON (*Amer. J. Physiol.*, 1909, 25, 199—203).—If the eggs are treated with hydrogen peroxide, much more oxygen is set free by eggs which have been fertilised than by unfertilised eggs. The maximum is reached in twenty minutes after fertilisation. The increase in catalase is due either to a kinase in the sperm cell, or by an increase in the permeability of the egg, so that peroxide and catalase come more easily together. W. D. H.

[Analyses of Brains. Distribution of Sulphur in Brains.] WALDEMAR KOCH (*J. Amer. Chem. Soc.*, 1909, 31, 1329—1335). WALDEMAR KOCH and FRED. W. UPSON (*ibid.*, 1355—1364).—See this vol., ii, 78, 79.

The Action of Certain Salts on Frogs' Motor Nerves. G. LILJESTRAND (*Skand. Archiv. Physiol.*, 1909, 22, 339—348).—Magnesium sulphate and chloride paralyse the motor nerves of the frog, but this occurs late and is preceded by a stimulating action. Weak solutions are not stimulating. Sodium chloride has a similar action. Zinc chloride acts in the same way, but much more strongly. W. D. H.

Influence of Different Substances on the Gaseous Exchange of the Surviving Muscular Tissue of Frogs. I. and II. TONSTEN THUNBERG (*Skand. Archiv. Physiol.*, 1909, 22, 406—429, 430—436).—I. The measurements were made by means of the author's micro-respirometer, generally in an atmosphere of oxygen. In the intact muscular tissue, the gaseous exchange is less than that of muscular tissue which has been cut by scissors; it is greater, however, than in muscular tissue which has been ground up with sand, so as to destroy the cell structure. Previous extraction of the tissue with physiological saline caused a marked diminution of the gaseous exchange; with isotonic neutral potassium phosphate, the diminution was less. The maximum of gaseous exchange takes place in isotonic saline; increase in the salt concentration causes a rapid diminution. There is not much difference in the gaseous exchange when the measurement is made after treatment with solutions of chlorides of the different alkali metals; the chlorides of the alkaline earths, on the other hand, cause considerable diminution. The action of the potassium halide salts is similar, with the exception of the fluoride, which causes a marked diminution in the gaseous exchange.

II. Oxalic, malonic, and succinic acids in the form of their potassium salts affect the gaseous exchange, considerably diminishing more especially the carbon dioxide output. The respiratory quotient is consequently affected by these salts. Other acids investigated do not affect the respiratory quotient in this manner.

S. B. S.

The Formation of Carbon Dioxide in Surviving Tissues. OLAV HANSEN (*Biochem. Zeitsch.*, 1909, 22, 433—441).—The author gives a method for estimating the carbon dioxide evolved by surviving tissues (chiefly liver) when suspended in physiological saline at 37°. The influence of antiseptics and other substances on the action was determined. Certain substances, such as sodium β -hydroxybutyrate, caused increased carbon dioxide output. Sodium lactate caused a slight increase. Most other sodium and ammonium salts had but little action; sodium glycollate, however, inhibited the output.

S. B. S.

Water Rigor in Frog's Muscle. EDWARD B. MEIGS (*J. Physiol.*, 1909, 39, 385—390).—The statement of du Bois Reymond, that in water rigor of frog's muscle, as in other forms of rigor, sarcosolactic acid is formed, was confirmed by the thiophen test. If the muscle is then placed in Ringer's solution, it loses acid and lengthens. This is regarded as a confirmation of the view that the acid is the cause, not the result or accompaniment, of the shortening.

W. D. H.

Action of Cinchona Alkaloids on Muscle. VICTOR H. VELEY and AUGUSTUS D. WALLER (*Proc. physiol. Soc.*, 1909, xix—xxi; *J. Physiol.*, 39).—The relative toxicity of poisons can be well studied by their effect on the direct excitability of the frog's sartorius. In the case of the alkaloids examined, the figures obtained are: cinchonamine 400, quinine 100, quinidine 50, cinchonine and cinchonidine 25. These figures agree very well with what would have been anticipated from physicochemical data.

W. D. H.

Extractives of Fish Muscle. FRIEDRICH KUTSCHER (*Zeitsch. physiol. Chem.*, 1909, 63, 104—105).—A reply to Suzuki and Yoshimura (*Abstr.*, 1909, ii, 910).—The base, $C_5H_{11}O_2N$, isolated from *Ommastrephes* sp., agrees in properties with betaine and not with δ -aminovaleric acid, as stated by these authors. Furthermore, other bases described by them, such as arginine, leucine, lysine, and proline, have already been isolated in the author's laboratory from extracts of sea and land animals.

S. B. S.

The Occurrence of Inactive Lactic Acid in a Meat Extract. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1909, 63, 237—247).—Valentine's meat juice has a minimal nutritive value. Its colour is due to a pigment which was not identified, but is possibly a derivative of hæmoglobin. When kept, it deposits a crystalline precipitate of magnesium salts, among which lactate is present. The lactic acid is of the optically inactive kind. The freshly prepared juice contains sarcosolactic acid, but as time goes on this is converted

almost completely into the inactive variety. Attempts to determine the cause of the transformation did not yield any certain results.

W. D. H.

The Nucleo-protein of Spleen. T. SATO (*Biochem. Zeitsch.*, 1909, 22, 489—494).—The nucleo-protein was prepared by precipitating the hot-water extract of the organ with dilute acetic acid. The amount of iron in various preparations varied between 0.15 and 0.80%. The metal appears to be contained in the nucleoprotein in two forms, namely, in a labile form, the part corresponding with which is removable from the substance by treatment with sodium carbonate, and a more stable form.

S. B. S.

Chemico-physical Investigations on the Crystalline Lens.
XI. Imbibition of the Lens in Water at Different Temperatures and in Acids and Alkalis. FILIPPO BORTAZZI and NOÉ SCALINCI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 327—339. Compare *Abstr.*, 1909, ii, 502).—The velocity and total amount of imbibition of the crystalline lens in water are greater at high than at low temperatures. Imbibition in dilute solutions of an acid or an alkali increases with the concentration of the solution. In solutions of various acids and of sodium hydroxide, imbibition increases in the following order: acetic acid, sulphuric acid, water, hydrochloric acid, and sodium hydroxide. Since, in the concentrations employed, these acids are completely dissociated, the sulphuric and acetic anions must exert a specific depressing influence on the imbibition, in opposition to the action of the hydrogen ions which increase the imbibition. A similar relation probably holds with solutions of different bases, the accelerating influence of the hydroxyl ions on the imbibition being modified to varying extents according to the nature and valency of the cation.

When immersed in the acid solutions employed, the lens becomes opaque, probably owing to the precipitation of the faco-protein, which in its natural state is an electro-negative colloid, by the hydrogen ions. This action is more marked with sulphuric and acetic acids than with hydrochloric acid, which seems to be capable of transforming the alkaline faco-protein rapidly into acid.

T. H. P.

Chemico-physical Investigations on the Crystalline Lens.
G. QUAGLIARIELLO (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 380—383).—The author has studied the influence of hydrochloric acid on the coagulation of the crystalline lens by the method previously employed with sodium hydroxide (*Abstr.*, 1909, ii, 1036).

The curve of the velocity of coagulation in presence of hydrochloric acid is essentially similar to that obtained with sodium hydroxide, the variation in the velocity gradually diminishing as the amount of acid is increased; in this case, however, the final value of the velocity differs far less from the initial value than is the case when sodium hydroxide is present. Whilst the latter, up to a certain concentration, first increases and then sensibly diminishes the velocity of coagulation, hydrochloric acid produces a continuous increase.

The results indicate that the influence of chemical agents on the

velocity of coagulation of the crystalline lens is a function of the superficial area of the lens.
T. H. P.

Chemical Investigation of Teeth. II. TH. GASSMANN (*Zeitsch. physiol. Chem.*, 1909, 63, 397—400. Compare Abstr., 1908, ii, 609).—Teeth from prehistoric men (at least 2000 years old) were found to be well preserved. They contain 3% more organic substance than recent teeth, and less magnesium and phosphoric acid. The percentage of calcium, sodium, potassium, chlorine, and carbon dioxide is the same as in recent teeth.
W. D. H.

Inorganic Constituents of Two Egyptian Mummies. PAUL HAAS (*Chem. News*, 1909, 100, 296).—The constituents of the ash were as follows:

	CaO.	K ₂ O.	Na ₂ O.	Fe ₂ O ₃ .	Al ₂ O ₃ .	CO ₂ .	SO ₃ .	P ₂ O ₅ .	Cl.	SiO ₂ .	
Mummy A	4.83	1.21	0.24	0.156	0.134	2.64	1.91	1.57	0.22	—	percent.
Mummy B	0.90	0.77	9.03	0.27	0.96	traces	2.69	0.42	1.89	5.80	"

A hot-water extract of "A" had an acid reaction, and the same material yielded to ether 9% of extract, which was acid and soluble in potassium hydroxide solution. No arsenic, antimony, or mercury was present. The high percentage of lime in the ash from "A" may indicate that quicklime was added to the coffin in which the body was placed.

Material "B," unlike "A," was moist, and lost 16% of its weight when dried at 100°, but the dry material rapidly increased in weight on exposure to air. The ether extract amounted to 3.5%. In this case the embalming material may have been "natron," or "nitrum," a mixture of sodium chloride, sulphate, and carbonate. Alumina has not been recorded previously as a constituent of mummy ash.

T. A. H.

Presence of an Anæroxydase and Catalase in Milk. J. SARTHOUS (*Compt. rend.*, 1909, 149, 809—810.* Compare Bordas, Abstr., 1909, ii, 505).—The filtrate from milk curdled at 30° gives a very distinct reaction with *p*-phenylenediamine, but not with guaiacol or hydrogen peroxide. By treating the residue on the filter with water, a liquid is obtained which gives distinct colorations with *p*-phenylenediamine and guaiacol in presence of oxygen. The casein, after having been freed from the anæroxydase by washing, reacts with *p*-phenylenediamine and hydrogen peroxide, but not with guaiacol.

The conclusions drawn are that milk contains a soluble anæroxydase as well as an insoluble catalase, and that the excessive sensitiveness of *p*-phenylenediamine to oxidation should be recognised in the study of oxidising ferments.
W. O. W.

Anæroxydase and Catalase in Milk. FRÉD. BORDAS and TOUPLAIN (*Compt. rend.*, 1909, 149, 1011—1012. Compare Abstr., 1909, ii, 505).—The author considers the experiments of Sarthou (preceding abstract) indecisive, since the colorations obtained were due to the presence of casein, which is always present in milk filtered

* and *J. Pharm. Chim.*, 1910, [vii], 1, 20—23.

through paper. When fresh or curdled milk is passed through the Chamberland filter, the filtrate gives no coloration with Storch's reagent. There is no evidence, therefore, of the presence of a soluble aneroxydase or insoluble catalase in cows' milk. W. O. W.

Can the Radium Emanations taken up by Drinking be Detected in the Urine? WALTHER LAQUER (*Chem. Zentr.*, 1909, ii, 854; from *Zeitsch. expt. Path. Ther.*, 1909, 8, 868—878).—By the method employed, emanations of less than 20,000 units cannot be detected in urine. The quantity of emanation in urine increases with the quantity in the water drunk. All the values found must be multiplied by 2. The urine voided in the first half hour contains only three quarters to four-fifths of the total excreted in the urine. The ratio of the quantity of emanation excreted to that ingested is about 1:4000. S. B. S.

The Origin of Ethereal Sulphates in the Organism. T. SATO (*Zeitsch. physiol. Chem.*, 1909, 63, 378—396).—Rabbits were treated with phenol added to their diet (cabbage), and certain sulphur compounds also added. The nitrogen and sulphur (in various combinations) were estimated in the urine. Isethionic acid only slightly raises the output of ethereal sulphates, and has no effect on nitrogen. It appears to be rapidly excreted. Cystine raises the total sulphates, and the amount of ethereal sulphate is parallel to this. Albumose prepared from egg-albumin has no action. Sulphidal (a colloidal sulphur preparation) enormously increases both total and ethereal sulphate excretion. Thiocarbamide is largely excreted as such; the effect on the excretion of sulphates is doubtful; the urine does not show the reactions of thiosulphuric acid. W. D. H.

The Origin and Destiny of Cholesterol in the Animal Organism. VI. The Excretion of Cholesterol by the Cat. G. W. ELLIS and JOHN A. GARDNER (*Proc. Roy. Soc.*, 1909, B, 81, 505—515. Compare Abstr., 1909, ii, 595).—The tendency for the change of cholesterol of food to coprosterol in faeces appears to be greater in cats than in dogs. In experiments with two cats on a diet of sheep's brain, coprosterol free from cholesterol was recovered; on a meat diet the change was not complete; on vegetable diet and on an artificial diet, as free as possible from cholesterol or phytosterol, no faecal coprosterol was found. A discussion of the part played by the cholesterol in the animal economy follows. G. S. W.

The Biological Significance of Lecithin. IV. The Blood-Content of Phosphorus and Iron in Lipoid Form in Cases of Polycythaemia rubra megalosplenica. W. GLIKIN (*Biochem. Zeitsch.*, 1909, 22, 461—463. Compare Abstr., 1909, ii, 1038).—The lecithin content was found to be about 5 grams per 1000 c.c. in cases of this disease as compared with 2 to 3 grams per 1000 as found by Abderhalden in the blood of mammals normally. The phosphorus and total iron were also large as compared with that found in normal cases. S. B. S.

The Detection of Phosphorus and Hypophosphorous Acids in Organs after Phosphorus Poisoning. II. RICHARD EHRENFELD and WILHELM KULKA (*Zeitsch. physiol. Chem.*, 1909, 63, 315—322. Compare Abstr., 1909, ii, 345).—Further investigations showed that during putrefactive processes the phosphorus is, in part, rapidly converted into phosphorous and hypophosphorous acids, but after this the change progresses but little. The experiments recorded further indicate that the normal phosphorised constituents of the body do not give rise to the acids mentioned. W. D. H.

***d*-Suprarenine (*d*-Adrenaline).** N. WATERMAN (*Zeitsch. physiol. Chem.*, 1909, 63, 290—294).—Previous work on the superior physiological activity of *l*-adrenaline is confirmed; so also is Abderhalden's work on so-called adrenaline immunity. Administration of the *d*-compound increases the resistance of mice towards the *l*-variety. W. D. H.

The Antagonism between Adrenaline and the Chlorides of the Alkaline Earths and of Potassium. THEODOR FRANKL (*Pflüger's Archiv*, 1909, 130, 346—352).—The action of adrenaline in stimulating sympathetic nerve-endings is antagonised by the chlorides mentioned in the title, of which the strongest is barium chloride. Sodium chloride has no such action. W. D. H.

Mode of Action of Nicotine and Curare, determined by the Form of the Contraction Curve and the Method of Temperature-coefficients. A. V. HILL (*J. Physiol.*, 1909, 39, 361—373).—From a mathematical consideration of the curves of contraction and relaxation of muscles under the influence of curare and nicotine at different temperatures, the conclusion is drawn that there is a combination between the drug and some constituent of the muscle. Evidence is also adduced for the existence of two or more types of fibres (or contractions) in the muscle selected for experiment, the *rectus abdominis* of the frog. W. D. H.

Relative Toxicity of Various Salts and Acids towards *Paramecium*. LORANDE LOSS WOODRUFF and HERBERT HORACE BUNZEL (*Amer. J. Physiol.*, 1909, 25, 190—194).—The experiments with some exceptions indicate a marked parallelism between the order of toxicity of various cations and their ionic potential. The high migration velocity of hydrogen ions will explain their unexpectedly high toxicity. Specific affinities of the living cell for certain ions will explain other exceptional cases, for instance, the low toxicity of copper. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Degradation by Bacteria of the Ultimate Hydrolysis Products of Proteins. WALTHER BRASCH (*Biochem. Zeitsch.*, 1909, 22, 403—406).—The degradation of various amino-acids by *Bacillus putrificus* and by mixed putrefying bacteria was investigated. Aspartic acid yields with mixed cultures propionic acid as chief product, together with small quantities of succinic acid. The pure culture gave the same products, together with small quantities of formic acid. Serine yielded both with pure and mixed cultures propionic acid with small quantities of formic acid. Tyrosine yielded with the pure culture *p*-hydroxyphenylpropionic acid. Glycine with the pure culture yielded acetic acid, alanine yielded propionic acid, and aminobutyric acid yielded butyric acid. S. B. S.

Accumulation of Nitrogen in Soils by Free Bacteria. ALFRED KOCH (*J. Landw.*, 1909, 57, 269—286. Compare Abstr., 1908, ii, 56).—A continuation of the experiments made in 1905 and 1906 (*loc. cit.*) on the effect of sugar on fixation of nitrogen by *Azotobacter*. The results show a considerable after-effect, increased yields of buckwheat, oats, and wheat being obtained in 1907, 1908, and 1909, and that the increased yields diminish regularly each year.

Experiments with sand inoculated with soil showed a gain of 7.2 mg. N per 100 grams in four months when sugar was added; and vegetation experiments with buckwheat grown in sand showed a very greatly increased production of dry matter (98.1 grams) in presence of sugar as compared with the amount obtained without sugar (23.7 grams), whilst the amounts of nitrogen in the produce were 409 and 54 mg. respectively.

Further experiments in plots ($\frac{1}{2}$ square metre) with wheat, rye, and oats (in 1907, 1908, and 1909) showed that the nitrogen fixed in the first year was only utilised to a slight extent, whilst the yields were considerably increased in the second and third years.

The examination of fifteen different soils showed that *Azotobacter* was present in seven of them, whilst eight gave negative results. The latter included three light, sandy soils, peaty, light and heavy soils, and soil from a pine wood. Addition of sugar to three of these soils failed to produce an increase in the nitrogen content.

Experiments are described in which mannitol, dextrose, calcium succinate, glycerol, calcium butyrate (10 grams each), and xylan (5 grams) were added to soil (500 grams) which was kept for a month at 25°. The soil with mannitol and with dextrose gained 12.3 and 6.9 mg. nitrogen per 100 grams respectively, whilst the others lost nitrogen (0.8 to 5.3 mg.). N. H. J. M.

Production of Citric Acid by Citromyces. PIERRE MAZÉ (*Ann. Inst. Pasteur*, 1909, 23, 830—833).—Citric acid is produced, not only when there is a deficiency of nitrogen, but also when any one of the

indispensable substances (phosphorus, potassium, iron or zinc, etc.) is absent *or deficient. A mineral solution, in which iron or zinc is wanting, gives on addition of sucrose (10%) a very insignificant amount of growth. It will, however, produce in a few weeks relatively important amounts of citric acid.

The mechanism of the formation of citric acid is discussed (compare Buchner and Wüstenfeld, Abstr., 1909, ii, 602). N. H. J. M.

Fungi which Produce Citric Acid. CARL WEHMER (*Chem. Zeit.*, 1909, 33, 1281).—In 1892 the author discovered two moulds which can convert sugar into citric acid (Abstr., 1893, ii, 591). Since then the number has been extended, and he has now isolated five or six others, morphologically much alike, capable of effecting the same change. *Citromyces Tollensianus* is characterised by its snow-white appearance in mass culture, although microscopically it differs but little from the others. Another species possesses the remarkable property of thriving in a saturated solution of oxalic acid (containing about 10% of acid); the hardiest mould previously known (*Aspergillus niger*) can only withstand about 1%, whilst most organisms are adversely affected by a trace. Another organism gives rise to oxalic instead of citric acid, but some oxalic acid (or rather its calcium salt) is always found in old cultures as a decomposition product of the citrate. E. J. R.

Theory of Disinfection. I. The Disinfecting Action of Phenol III. HEINRICH REICHEL (*Biochem. Zeitsch.*, 1909, 22, 201—231. Compare Abstr., 1909, ii, 1045).—The assumption is made that the disinfecting action depends on the coefficient of distribution of the disinfectant between the two phases, namely, the bacteria and the disinfecting solution. The disinfecting action of phenol in the presence of varying quantities of sodium chloride was determined, suspensions of typhus bacilli and staphylococci being employed. The time of exposure to the solutions just necessary to kill the cultures was determined, the method of sub-culturing being employed. The curves obtained were submitted to mathematical analysis, and the factors influencing the distribution of the disinfectant between two phases, such as imbibition of water by the protein, etc., discussed. S. B. S.

Influence of Varying Relations between Lime and Magnesia on the Growth of Plants. LUIGI BERNADINI and A. SINISCALCHI (*Chem. Zentr.*, 1909, ii, 857; from *Staz. sper. agrar. ital.*, 1909, 42, 369—386).—The injurious effect of an excess of calcium and the poisonous action of an excess of magnesium do not depend on the absolute amounts of calcium and magnesium ions taken up, but on the relation of the amounts absorbed by the plant to each other. The assimilated phosphoric acid is a function of the relation CaO/MgO in the nutritive medium, and depends on the relation of the calcium and magnesium ions in which these are absorbed. N. H. J. M.

Formation of Starch from Sorbitol in Rosaceæ. O. TREBOUX (*Ber. Deut. bot. Ges.*, 1909, 27, 507—511).—Experiments with

numerous varieties of *Pomoideæ*, *Prunoideæ*, *Spiraeoideæ* showed that all of them are able to produce starch from sorbitol, whilst negative results were obtained with two other sub-orders, *Rosoidæ* and *Ruboidæ*, and with the related orders of the *Saxifraginæ* and *Leguminosæ*. None of the plants which produce starch from sorbitol are able to utilise mannitol and dulcitol.

As compared with sugars and glycerol, the production of starch from sorbitol is almost always much more vigorous.

Sorbitol has up to the present only been found in fruits, but further investigation will probably show that it occurs in leaves and other parts of plants.

N. H. J. M.

Influence of Aluminium Salts on the Colour of Flowers
VALENTIN VOUK (*Bied. Zentr.*, 1909, 38, 755—756; from *Oesterr. bot. Zeitsch.*, 1909, 58, 236—243).—Plants of *Hydrangea hortensis* watered with a 3% solution of alum produced flowers of a fine blue colour; at the same time brown spots appeared on the leaves, which died at an early stage. The best results were obtained with 1% solutions, which had no injurious effect, whilst the production of blue flowers was nearly complete. When aluminium sulphate was employed, the coloration was less strong.

Experiments with *Phlox decussata* gave negative results.

N. H. J. M.

Protective Action of Sodium for Plants. W. J. V. OSTERHOFF (*Bied. Zentr.*, 1909, 38, 730—731; from *Jahrb. wiss. Bot.*, 1908, 43, 121—136).—Water and soil culture experiments in which roots, algae, and moulds, etc., were supplied with single salts and with mixtures showed that the poisonous action of calcium is diminished by addition of small amounts of a sodium salt. The antagonism between sodium and calcium salts is stronger than between sodium, magnesium, and potassium salts.

The conclusion is drawn that sodium is not a nutrient, but a protective substance for plants, and probably for animals. Salts of aluminium, zinc, and cobalt have a protective action for animals, and salts of calcium for fungi.

N. H. J. M.

Molecular Complexity of Caoutchouc in the Milk. F. WILLY HINRICHSSEN and ERICH KINDSCHER (*Ber.*, 1909, 42, 4329—4331).—The form in which caoutchouc occurs in the milk of caoutchouc-yielding plants is still unknown, Weber claiming that the milk contains a hydrocarbon, $C_{20}H_{32}$, which polymerises to caoutchouc during the technical preparation of the substance (*Abstr.*, 1903, i, 845), whilst de Jong and Tromp de Haas (*Abstr.*, 1904, ii, 782) assert that caoutchouc occurs already prepared in the milk; Harries also holds the latter view (*Abstr.*, 1904, i, 1038). The authors have centrifugalsed *Kickxia* milk with pure benzene until an approximately clear solution is obtained containing the caoutchouc and the caoutchouc-resin. The depression of the freezing point of this solution is determined; the residue is weighed after evaporation of the solvent, and extracted with acetone to remove the resin. The mole-

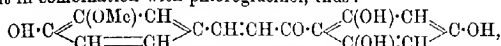
cular weight of the latter in benzene is 426, and by calculation the molecular weight of the compound is found to be 3173, a result which does not support Weber's view.

C. S.

Influence of Anaesthetics and of Cold on Coumarin-producing Plants. ÉDOUARD HECKEL (*Compt. rend.*, 1909, 149, 829—831. Compare Guignard, Abstr., 1909, ii, 823; Mirande, *ibid.*, ii, 824).—The odour of coumarin in plants, such as *Anthoxanthum odoratum* or *Melilotus officinalis*, is only perceptible in the dried leaf, but is rapidly developed in the living leaves when these are submitted to the action of anaesthetics or of cold. The author confirms the generality of similar phenomena observed by Guignard in the case of Cruciferae, and has extended the experiments to *Lepidium latifolium* and *Cochlearia armoracia*.

W. O. W.

Ajuga Iva. UGO PONTI (*Gazzetta*, 1909, 39, ii, 349—353).—The plant *Ajuga Iva*, which is largely employed in the neighbourhood of Sassari as a remedy for malarial fever, contains no alkaloids, but, on distillation in a current of steam, yields a small quantity of a green oil having a characteristic aromatic odour. When treated with milk of lime, the herb yields ferulic acid, which probably exists in the plant in combination with phloroglucinol, thus:



this structure being analogous to that of homoeiodictyol (compare Power and Tutin, *Trans.*, 1907, 91, 887).

T. H. P.

Presence of Aucubin in Different Varieties of Aucuba Japonica. C. LEBAS (*J. Pharm. Chim.*, 1909, [vi], 30, 390—392).—Six garden varieties of this plant, namely, *elegantissima*, *latimaculata*, *longifolia*, *punctata*, *salicifolia*, and *viridis*, have been examined and found to contain aucubin (Bourquelot and Hérissé, Abstr., 1902, i, 634), which was isolated in the manner described already (*loc. cit.*). The quantity obtained varied from 0.3% for *elegantissima* to 1.9% for *latimaculata*.

T. A. H.

Occurrence of a Cyanogenetic Glucoside in Linaria Striata. ÉMILE BOUQUELOT (*J. Pharm. Chim.*, 1909, 30, 385—389).—The plant was extracted with alcohol, and the concentrated extract dissolved as far as possible in an aqueous solution of thymol. This aqueous extract contained (1) sucrose, identified by its resolution into "invert sugar" by the action of invertase, and (2) a cyanogenetic glucoside, hydrolysed by emulsin into benzaldehyde, hydrogen cyanide, and a reducing sugar, probably dextrose. The amount of dextrose produced was in excess of that required for any known glucoside producing benzaldehyde, so that probably a second glucoside was present in the extract.

T. A. H.

Existence of Two New Glucosides, Decomposable by a Ferment, in Primula officinalis. A. GORIS and MASCRÉ (*Compt. rend.*, 1909, 149, 947—950).—The fresh roots of *Primula officinalis*,

like those of other species of *Primula*, emit a characteristic odour when bruised. This appears to be due to interaction between two glucosides and an enzyme, for which the name *primeverase* is suggested. The new ferment has been shown not to be identical with emulsin, myrosin, or betulase. Details are given of the method employed in isolating the glucosides, *primeverin* and *primulaverin*. The former occurs in colourless crystals, m. p. 172—173°, $[\alpha]_D - 60.24$, whilst the latter forms needles, m. p. 160—161°, $[\alpha]_D - 66.86$. Both are hydrolysed by dilute sulphuric acid, disengaging an odour of anise and furnishing a substance which, in the case of primeverin, develops a bright blue coloration with ferric chloride and a lilac-violet coloration in the case of primulaverin. W. O. W.

Localisation of Proteolytic Ferments in *Vasconcellea quercifolia*. The Rennet and Spontaneously Coagulable Latex. C. GERBER (*Compt. rend.*, 1909, 149, 737—740. Compare Abstr., 1909, ii, 512, 824).—Unlike the majority of plants, the foliaceous ribs of *Vasconcellea quercifolia* show greater rennet activity than the parenchyma. Other parts of the plant show similar divergence from the general rule. This appears to be connected with the proportion of latex in the organs, since, for example, the ribs are richer in latex than the parenchyma. On the other hand, the presence of a milky latex, such as that of the chestnut, is not invariably associated with marked proteolytic activity. The rennet activity of *V. quercifolia*, *Funtumia elastica*, *Artocarpus incisa*, and *A. integrifolia* shows some proportionality to the readiness with which the sap undergoes spontaneous coagulation. W. O. W.

Action of Different Amounts of Copper in the Soil on the Growth of Plants. J. SIMON (*Landw. Versuchs.-Stat.*, 1909, 71, 417—429).—Mustard and barley were grown in a mixed soil, in sand, in garden soil, and in a clay soil, to which small amounts of copper sulphate were added. In the mixed soil the yield of mustard was reduced by about 11—13% by 0.001 and 0.01% of copper sulphate and to 23 and 0.3% by 0.1 and 0.5% respectively, whilst the plants were killed by 1%. Barley is less sensitive, being unaffected by 0.001% of copper sulphate and remaining alive in presence of 1%. With regard to the sand and other soils, the experiments showed that copper sulphate is most poisonous in sand and least in the garden soil.

Experiments on the absorptive power of the soils showed that 100 grams of the garden soil absorbed 1.252 grams of copper sulphate, whilst the mixed soil and the clay soil absorbed 0.378 and 0.111 respectively, and the sand none at all. N. H. J. M.

Deposition of Nitrogen in Full-grown Animals with Abundant Food. KURT FRISKE (*Landw. Versuchs.-Stat.*, 1909, 71, 440—482).—The results of the experiments of Lawes and Gilbert (*Phil. Trans.*, 1859, 493) on the changes in the composition of animals when fattened, showed that the gain is chiefly in fat (two-thirds) and water (one-fourth), and includes only a very small amount of nitrogenous matter. The experiments were made chiefly with young

animals. More recent experiments, with fully-grown animals, have also indicated, on the whole, that the gain in animals when fattened consists almost exclusively of fat.

In the experiments now described, eight full grown sheep (over four years old) were fed for six months on moderate amounts of hay. They were then shorn, weighed, and two of them killed and analysed. Two of them were then fed for about one hundred days on a nitrogenous diet of hay (450), beans (300), and sunflower cake (260 grams per day). The nutritive ratio was 1:2.88. Two others were fed with a less nitrogenous diet (1:5.02), consisting of hay (450), beans (270), and crushed barley (290 grams per day). The remaining two were reserve sheep which were not, however, required.

At the commencement, in the middle, and at the end of the fattening period, the sheep were kept for ten to eleven days in stalls for the collection of urine and faeces, which were weighed and analysed. Finally, the animals were again shorn, weighed, and then analysed.

The analytical results showed that, during fattening, the sheep put on considerable amounts of flesh, the greater gain being in the sheep with the nutritive ratio 1:5.02. The results of the balance experiments indicated a greater deposition of nitrogenous matter than the direct analysis.

The gain in fat was greater than the gain in flesh in both experiments.
N. H. J. M.

Soil Analysis. JAMES HARVEY PETTIT (*J. Landw.*, 1909, 57, 237—267; from *Inaug. Diss. Göttingen*, 1909).—The method of Schloesing and von Sigmond was employed with six different soils. The results showed very clearly a definite natural limit of solubility for phosphoric acid; and when the basicity of the soil is allowed for, the concentration of acid which acts uniformly lies between fairly definite limits, 400—800 mg. N_2O_5 per litre. The method also makes distinction between readily soluble and sparingly soluble potash, but a uniformly acting concentration was only found in the case of the loam.

The relation between the percentages of total phosphoric acid and total potash is not the same as the relation between the amounts soluble in dilute nitric acid. Muschechalk contains more total but much less readily soluble phosphoric acid than Buntsandstein.

The results of vegetation experiments agreed with the soil analyses in the case of loam and Muschechalk soils.

The amounts of phosphoric acid and potash assimilated by barley, beans, buckwheat, and potatoes are not the same as the amounts dissolved by dilute nitric acid. The different plants, moreover, take up very different amounts of these substances—buckwheat assimilated 3.5 times as much potash and twice as much phosphoric acid as barley; so that no one solvent can possibly indicate the amounts of nutritive substances available to all plants. It is therefore desirable to employ the term “readily soluble” instead of “available.”

N. H. J. M.

Analytical Chemistry.

Improved Method of Collecting Gases from the Mercury Pump. FREDERICK G. KEYES (*J. Amer. Chem. Soc.*, 1909, 31, 1271—1273).—In the ordinary method of collecting gases from the mercury pump in an inverted tube and transferring them to the gas analysis apparatus, minute bubbles of air are liable to be trapped even when great care is exercised. The following arrangement has been devised in order to avoid this source of error. A wide tube for collecting the gases is sealed on to the up-turned end of the capillary tube of the pump. The wide tube is provided at the lower end with a side-tube, which is connected to a reservoir of mercury by means of rubber tubing. The upper end of the wide tube bears a three-way stopcock furnished with capillary leads. Towards the end of an ordinary exhaustion, the air in the wide tube can be expelled by raising the reservoir. On closing the stopcock and lowering the reservoir, a vacuum is formed in the tube, into which the bubbles passing down the pump capillary will be discharged. The method of employing the apparatus for the collection of gases is very simple, and is described with the aid of a diagram. E. G.

Automatic Filling Burette. R. FRAILONG (*Bull. Assoc. Chim. suc. dist.*, 1909, 27, 470—471).—A description of two kinds of automatic burettes, one intended to deliver a definite quantity of reagent at once, and the other for delivering the same drop by drop.

The main parts of the apparatus are a reservoir with a tube supplying the burette, a specially-constructed Mohr's pinchcock, which serves to open the outlet tube while closing simultaneously the supply tube, and a capillary tube passing through the rubber cork of the burette and dipping slightly into the liquid; it serves to obtain the zero point automatically. L. DE K.

Apparatus for the Rapid Electro-analytical Separation of Metals. HENRY J. S. SAND (*Trans. Faraday Soc.*, 1909, 5, 159—164).—A description of some developments made in the author's apparatus for the rapid electro-analysis and separation of metals (compare *Trans.*, 1907, 91, 373; 1908, 93, 1572).

A special screw-cap has been provided, which may be screwed down when the apparatus is not in use, making it possible to transport it without taking out the mercury which is employed to make connexion between the stationary and moving parts in the electrolytic stand. A clutch arrangement has also been added, which enables the operator to start or stop the rotation of the anode without stopping the motor.

All the apparatus required for the measurement of the electrode potential is now fitted into a single box. The arrangement is so designed that by depressing a key it will also allow the potential difference between the anode and the cathode to be read directly. The

capillary electrometer is retained as a zero instrument, and a special portable form, which is a modification of the Ostwald horizontal capillary electrometer, has been designed. It is provided with an enclosed scale, and will readily indicate one millivolt when observed with a lens.

T. S. P.

Aluminium Dishes and other Appliances in Quantitative Analysis. JAROSLAV FORMÁNEK and FRANZ PEČ (*Chem. Zeit.*, 1909, 33, 1282—1283).—Dishes of aluminium may be substituted for those of platinum in electrolytical separations, but it is necessary to have the inside of the dish plated with a very thin sheet of copper. This may then in turn be coated electrolytically with tin or silver, etc., according to circumstances. A number of successful experiments are communicated. Several improved appliances for quick electrolytic estimations are also described.

L. DE K.

Electrolytic Estimation of Chlorine in Hydrochloric Acid with the Use of a Silver Anode. FRANK A. GOOCH and H. L. READ (*Amer. J. Sci.*, 1909, [iv], 28, 544—552; *Zeitsch. anorg. Chem.*, 1909, 64, 287—297).—The authors have shown by a large number of experiments that when using anodes of silver or silver-plated platinum gauze and currents of various strengths, the results are not so satisfactory as might have been expected. This is caused by the fixing of oxygen as well as chlorine on the anode, the removal of silver from the anode to the cathode, and the formation of hypochlorous acid. Even when the anode is ignited to decompose silver oxides, the results are still irregular and always low.

L. DE K.

The Beilstein Reaction [for Halogens]. HUGO MILROTH (*Chem. Zeit.*, 1909, 33, 1249).—The author has shown that the Beilstein copper oxide flame test for halogens is not absolutely trustworthy, as, owing to the formation of cupric cyanide, a green coloration is occasionally noticed, which, although not quite so characteristic, may be mistaken for the halogen colour.

The reaction is given by picolinic acid, quinolinic acid, 2-methylpicolinic acid, dipicolinic acid, methyl 2-hydroxynicotinate, quinaldinic acid, and nicotinic acid, whereas no green flame was observed with quinoline, isoquinoline, isonicotinic acid, cinchoninic acid, cinchomeronic acid, methylantranilic acid, apophenylic acid, and papaveric acid.

In the case of hydroxyquinoline the reaction is obtained even without the use of a copper oxide bead.

L. DE K.

Analysis of Mixtures of Halogen Acids. II. WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1909, 31, 1273—1275. Compare Abstr., 1909, ii, 612).—The following method is recommended for the analysis of mixtures containing two halide ions. Silver nitrate is added in excess, and the precipitated silver salts are collected and weighed. The solution containing the excess of silver nitrate is titrated with thiocyanate and ferric nitrate by the Volhard method. It is shown that if a is the weight of silver nitrate required to precipitate both the halogens present, and b is the weight of silver

halides precipitated, the quantities of the halogens can be calculated by the following equations. For mixtures containing chlorine and bromine: $\text{Cl} = 0.8817a - 0.7976b$; $\text{Br} = 1.7976b - 1.5166a$. For mixtures containing chlorine and iodine: $\text{Cl} = 0.5358a - 0.3877b$; $\text{I} = 1.3877b - 1.1706a$. For mixtures containing bromine and iodine: $\text{Br} = 2.3501a - 1.7004b$; $\text{I} = 2.7007b - 2.9851a$.

Mixtures containing three halide ions can be analysed by the same method if one of the halogens is estimated separately. Thus, if iodine is estimated separately, we have $\text{Cl} = 0.8817a - 0.7976b$ ($+ 0.2954 \text{ I}$); $\text{Br} = 1.7976b - 1.5166a$ ($- 1.2951 \text{ I}$). If the bromine is estimated separately, $\text{Cl} = 0.5358a - 0.3877b$ ($- 0.2280 \text{ Br}$); $\text{I} = 1.3877b - 1.1706a$ (0.7720 Br). If the chlorine is estimated separately, $\text{Br} = 2.3501a - 1.7004b$ ($- 0.4386 \text{ Cl}$); $\text{I} = 2.7007b - 2.9851a$ ($+ 3.3857 \text{ Cl}$).

E. G.

Estimation of Perchlorates by means of Titanous Salts. VICTOR ROTHMUND and A. BURGSTALLER (*Chem. Zeit.*, 1909, 33, 1245).

—Contrary to Stähler's statement (*Abstr.*, 1909, ii, 699) that the estimation of perchloric acid by boiling with excess of titanous sulphate and then titrating with permanganate is unsatisfactory, the authors find that the results are trustworthy, provided the operation takes place in a flask fitted with a cooling arrangement, and in an atmosphere of carbon dioxide.

The chloride formed in the reaction may be estimated by way of a check, but the use of the nephelometer cannot be recommended in this case.

L. DE K.

Simple Process for the Estimation of Iodine. ERNST WINTERSTEIN and E. HERZFELD (*Zeitsch. physiol. Chem.*, 1909, 63, 49–57).—The apparatus consists of a 250 c.c. round-bottomed flask with a narrow neck, which is closed by means of a ground joint, through which pass two tubes, like those of an ordinary washbottle. The exit tube is also furnished with a ground joint, by means of which it is connected with a short condenser. The end of the condensing tube is connected with two absorption flasks filled half way with a 10% solution of potassium iodide.

Fifty c.c. of the solution to be tested for small quantities of iodides (bromides or chlorides do not interfere) are placed in the flask, together with 5 c.c. of phosphoric acid and 10–20 c.c. of commercial hydrogen peroxide. A current of air is drawn through the apparatus, and the solution is heated gradually to boiling. After thirty minutes the iodine is expelled and absorbed by the potassium iodide, and may be titrated.

When applying the process to urine, the results are only qualitative, but the full amount of iodine present may be obtained by rendering the urine alkaline with sodium hydroxide, evaporating to dryness, and destroying the iodised organic compounds by ignition.

L. DE K.

Estimation of Iodine in Organic Substances. VINCENZO PAOLINI (*Mon. Sci.*, 1909, [iv], 23, 648).—The following method is recommended for the estimation of iodine in such substances as blood,

urine, brain-substance, sea-weed, thyroid glands, etc. A particular instance is given of the estimation of iodine in iodoform-gauze. Ten grams of the gauze, cut into small pieces, are treated in a flask with 40 grams of zinc dust and 60 c.c. of 25% sulphuric acid. The mixture is heated by means of a water-bath in a reflux apparatus for about three hours, a further 50 c.c. of sulphuric acid being then added and the heating continued for some hours. The iodine present is thus converted into hydriodic acid. The gauze is then washed several times by decantation with water, and the solution made up to a volume of 1 litre. One hundred c.c. of this solution are treated with a few c.c. of potassium nitrite solution and extracted with 100 c.c. of carbon disulphide. The carbon disulphide is then separated, washed with water, and the iodine dissolved in it is titrated with standard thio-sulphate solution in the presence of sodium hydrogen carbonate.

W. P. S.

Estimation of Iodine in the Thyroid. ATHERTON SEIDELL (*J. Amer. Chem. Soc.*, 1909, 31, 1326—1329).—Riggs (Abstr., 1909, ii, 699) has stated that the estimation of iodine in the thyroid by Baumann's method (Abstr., 1896, ii, 487) is liable to error, owing to the formation of iodate during the fusion, and he has therefore suggested a modification involving a reduction process.

In the present paper, an account is given of experiments which indicate that Baumann's method is satisfactory, and that Riggs' modification is not only unnecessary, but actually leads to greater error than the original method, since it is difficult to remove the whole of the iodine from the aqueous layer before applying the reduction process, and any iodine remaining in solution renders the results inaccurate.

E. G.

Estimation of Sulphur Dioxide and Sulphuric Acid in the Gases of Sulphur Furnaces. HENRI PELLET (*Bull. Assoc. Chim. sucr. dist.*, 1909, 27, 468—469).—The author described his sulphur-carbonimeter some ten years ago in a pamphlet issued for private circulation, and now communicates some results obtained. The process is based on the fact that on passing the gases through water, the sulphuric acid is removed, the sulphur dioxide being absorbed by a suitable reagent contained in a second washbottle.

L. DE K.

Estimation of Dithionous Acid and Dithionates. HENRI BAUBIGNY (*Compt. rend.*, 1909, 149, 1069—1071. Compare Ashley, Abstr., 1906, ii, 800).—Preliminary experiments showed that it was not possible to oxidise dithionous acid completely to sulphuric acid by heating with *aqua regia*, either in open or closed vessels.

The solution containing the dithionate is mixed with a sufficient amount (12 to 15 times the quantity of dithionate present) of a mixture of sodium carbonate and nitrate. If a precipitate is formed, it is filtered off and washed; the filtrate and washings are then evaporated to dryness, and the residue carefully fused during from ten to fifteen minutes. The sodium sulphate so formed is estimated in the usual way with barium nitrate in presence of nitric acid.

T. A. H.

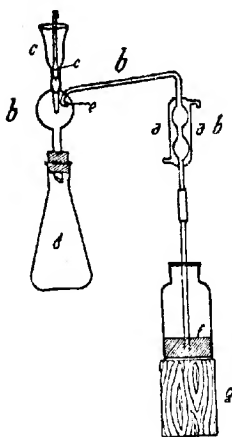
Estimation of Nitrogen in Soil Extracts. DENSCH (*Chem. Zeit.*, 1909, 33, 1249—1251).—A reply to Mitscherlich (*Abstr.*, 1909, ii, 935).—The author upholds the accuracy of his process, and prefers it to the more scientific method of Mitscherlich in the case of analysis of the aqueous extract of soils. For the reduction of the nitrates (any nitrite is first oxidised by means of permanganate) in acid solution, a mixture of iron and zinc powder is recommended, although iron alone may be used.

L. DE K.

Method of Estimating very Small Amounts of Nitrogen. T. ZELLER (*Landw. Versuchs.-Stat.*, 1909, 71, 437—440).—The method described by Mitscherlich, Herz, and Merres (*Abstr.*, 1909, ii, 614) is considered impracticable, owing to the relatively large and variable amounts of nitrogen unavoidably introduced in the reagents.

N. H. J. M.

New Distillation Arrangement for Ammonia Estimation. ADOLF BERTHOLD (*Chem. Zeit.*, 1909, 33, 1292).—By using this apparatus all loss of ammonia is avoided.



The substance is placed in the flask *d*, and the centre-piece *b* is put on. The receiver *f*, which contains the standard acid, is then raised by a wooden block *g* until the delivery tube dips into the acid. The funnel *c* is now filled with alkali, and by gently lifting the tube *e* the liquid is allowed to run into *d*, but a little should be left in the funnel so as to form a seal; the remaining alkali is then removed by rinsing a few times with water still retaining the seal. After connecting the condenser *a* with the water supply, the contents of *d* are heated over a Bunsen burner. When the distillation is practically finished, the wooden block is removed and the distillation continued for a short time.

When dealing with liquids containing free ammonia, these should be introduced through the funnel tube *c* after placing on the centre-piece and raising the receiver. Into *e* a drop catcher has been sealed.

L. DE K.

Estimation of very Small Amounts of Ammonia in Large Quantities of Air. PAUL LIECHT and ERNST RITTER (*Chem. Zeit.*, 1909, 33, 1265—1266).—The apparatus consists of a U-tube containing diluted *N*-sulphuric acid, one limb of which is attached to a vertical, spindle-shaped tube, which is connected to the first of two pipettes inclined at about 45° to the vertical; the top pipette is attached to a second U-tube. By means of a ventilating fan, the air is drawn very rapidly through the apparatus. The acid is swept

mainly into the spindle-shaped tube, where it is churned violently by the air current, and a good deal of the acid is converted into spray; this, however, settles on the walls of the two pipettes and flows back; it is found that practically every trace of ammonia is removed.

L. DE K.

New Arrangement for the Estimation of Nitric Compounds in Sulphuric Acid. K. LEO (*Chem. Zeit.*, 1909, 33, 1218—1220).—Instead of shaking the sulphuric acid with mercury (Lunge's process), 50 c.c. of the sample are placed in a specially constructed bulb, the remaining space being taken up with mercury. By means of a tube furnished with three openings and connected with a mercury pressure flask, mercury is forced into the acid like a spray, and the action soon starts. The mercury displaced runs into another reservoir, and from there into a beaker, and is afterwards emptied into the pressure flask. The nitric oxide liberated is then transferred to a gas volumeter and measured.

For working details the illustrations in the original article should be consulted.

L. DE K.

Reduction of Nitric Nitrogen to Ammonia; New Process for the Estimation of Nitrates. M. KEMMUEL POZZI-ESCOFF (*Bull. Assoc. Chim. suc. dist.*, 1909, 27, 457—459; *Ann. Chim. anal.*, 1909, 14, 445—446).—The nitrate is placed in a distilling flask fitted with a funnel safety tube, 5 to 6 grams of aluminium cuttings and 2 c.c. of a saturated solution of mercuric chloride are added, and also 150 to 200 c.c. of water. After connecting the flask with the condensing apparatus, a brisk evolution of hydrogen will be noticed; a solution of sodium hydroxide is added, and the ammonia formed is distilled off and collected as usual in standard acid. In order to decompose traces of ammoniated mercury compounds, a few c.c. of sodium hypophosphite solution are added towards the end.

L. DE K.

Modification of the Grandval and Lajoux Process for the Estimation of Nitrates in Waters Charged with Chlorides. L. FARCY (*Bull. Soc. chim.*, 1909, [iv], 5, 1088—1090).—The author stated previously that in the presence of chlorides the process used by Grandval and Lajoux failed to give correct results, and he constructed correction tables. By operating as follows, and using an improved reagent, the use of these tables may be avoided.

One volume of a mixture of 37 parts of sulphuric acid and 3 parts of phenol is mixed with 1 volume and a-half of hydrochloric acid and 1 volume and a-half of water, and heated for half an hour on the water-bath. The residue left on evaporation of the sample is moistened with 1 c.c. of the reagent and heated on the water-bath for fifteen minutes. The residue is then rendered alkaline with ammonia, and the coloration compared with that of a standard water similarly treated.

L. DE K.

Influence of Nitrites on the Estimation of Nitrates by Grandval and Lajoux's Process. L. FARCY (*Bull. Soc. chim.*, 1909, [iv], 5, 1090—1091).—The author states that, although nitrites do not themselves affect Grandval and Lajoux's reagent, the least trace of nitrate added gives a coloration far more powerful than would be expected.

The nitrite should therefore be estimated separately by means of Griess' reagent, and before estimating the nitrate it should be oxidised with permanganate, or else destroyed by means of carbamide.

L. DE K.

Influence of Chlorides on the Estimation of Nitrates. L. FARCY (*Bull. Soc. chim.*, 1909, [iv], 5, 1091).—The loss in nitrate observed when applying the Grandval and Lajoux colorimetric test for nitrates in presence of chlorine is due to the formation of nitro-hydrochloric acid; this may be proved by passing the gaseous products of the reaction through a solution of potassium iodide, when the amount of iodine liberated corresponds with the loss observed.

A slight mechanical loss owing to effervescence is also unavoidable.

L. DE K.

Coloured Substances Produced in Grandval and Lajoux's Reaction. MAURICE LOMBARD (*Bull. Soc. chim.*, 1909, [iv], 5, 1092—1096).—The coloration is mainly caused by a mixture of *o*-nitrophenol-*p*-sulphonic acid and *o*-nitrophenol. The latter substance gives a more intense red coloration with ammonia.

L. DE K.

Estimation of Mineral Constituents in Vegetable Substances. L. VUAFIART (*Bull. Assoc. Chim. suc. dist.*, 1909, 27, 454—456).—Polemical. A reply to Pellet (*Abstr.*, 1909, ii, 755) on the subject of the volatilisation of phosphoric compounds on incinerating vegetable substances. The errors are avoided by using the moist combustion process with sulphuric acid. The use of alcohol when estimating nitrates is also discussed, also the possibility of some magnesium ammonium phosphate remaining on the filter when dissolving the yellow molybdate precipitate in dilute ammonia containing some citrate solution.

L. DE K.

Estimation of Mineral Constituents in Vegetable Substances. HENRI PELLET (*Bull. Assoc. Chim. suc. dist.*, 1909, 27, 456—457).—Polemical. A further reply to Vuafart (preceding abstract). The author did use citrate solution, and not nitrate, as reported erroneously. Attention is called to the fact that the application of alcohol in the estimation of nitrates has already been advocated by Boussingault in 1865.

L. DE K.

Estimation of the Free Acid in Superphosphates. FREDERICK B. GUTHRIE and A. ALEXANDER RAMSAY (*J. Roy. Soc. New South Wales*, 1909, 43, 69—74).—The methods recommended for the estimation of free phosphoric acid have been examined. Herzfelder's method, in which the free acid is extracted with ether and titrated in aqueous solution with methyl-orange as indicator, gives the best results, but

the values obtained are rather low. A modification of this method, in which sodium alizarinsulphonate is used as indicator, will probably prove to be the best method of estimating free phosphoric acid in superphosphates.

H. M. D.

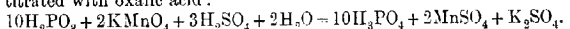
Estimation of Total Phosphoric Acid in Basic Slags and Native Phosphates by the "Citro-mechanic Method." E. GUERRY and E. TOUSSAINT (*Bull. Soc. chim. Belg.*, 1909, 23, 454—457).—Twenty to twenty-five c.c. of sulphuric acid are introduced into a 250 c.c. Jena flask by means of a funnel tube so as not to moisten the neck. 2.5 Grams of the powdered sample are added, and, after gently shaking, the whole is boiled for ten minutes. When cold, water is added a little at a time, and when cooled down, the solution is diluted to the mark, well shaken, and filtered. Twenty-five c.c. of the filtrate are placed in a beaker and neutralised with ammonia, and when cold, 30 c.c. of ammonium citrate solution (= 10 grams of citric acid) are added, followed by 15 c.c. of ammonia. After starting the stirring machine, 35 c.c. of magnesium mixture are added drop by drop, and, after twenty-five minutes, the precipitate is collected, washed with dilute ammonia, and ignited.

No correction need be made for the volume of the insoluble matter, as this contains relatively the same amount of phosphoric acid as the solution.

L. DE K.

Estimation of Hypophosphoric, Phosphorous, and Hypophosphorous Acids in Presence of One Another, and of Phosphoric Acid. ARTHUR ROSENHEIM and JAKOB PINSKER (*Zeitsch. anorg. Chem.*, 1909, 64, 327—341).—A method was required for the analysis of the acid obtained from the action of moist air on yellow phosphorus.

Hypophosphoric acid (the pure sodium salt was used) may be estimated by titration with permanganate if certain precautions are observed. The slightly acid solution, with the addition of a small quantity of permanganate, is heated to 80—90°, titrated rapidly with oxalic acid, more permanganate added, and so on, until a red coloration persisting for five minutes is obtained. The excess is then titrated with oxalic acid:



Iodine is without action on hypophosphoric acid. Uranyl salts give a yellow precipitate according to the equation: $2\text{NaHPO}_3 + \text{UO}_2(\text{NO}_3)_2 = \text{UO}_2(\text{HPO}_3)_2 + 2\text{NaNO}_3$.

Phosphorous acid may be estimated by means of permanganate under the same conditions as hypophosphoric acid. It reacts quantitatively with iodine, when heated in a closed flask, to form phosphoric acid, and may thus be estimated in the presence of hypophosphoric acid.

Hypophosphorous acid may be titrated with permanganate as above: $5\text{H}_2\text{PO}_2 + 4\text{KMnO}_4 + 6\text{H}_2\text{SO}_4 = 5\text{H}_3\text{PO}_4 + 4\text{MnSO}_4 + 6\text{H}_2\text{O} + 2\text{K}_2\text{SO}_4$, and also reacts quantitatively with iodine when heated in acid solution in a closed flask. In all cases the oxidation of any one acid is unaffected by the presence of one or more of the other acids. Jan

mixture containing phosphoric, phosphorous, hypophosphoric, and hypophosphorous acids may be analysed by (1) oxidising with nitric acid and precipitating with magnesia, thus estimating total phosphorous; (2) titrating with permanganate, which oxidises all but the phosphoric acid; (3) titrating with iodine, which oxidises only phosphorous and hypophosphorous acids; (4) titrating with uranyl nitrate, which precipitates only phosphoric and hypophosphoric acids. Equations for calculating the proportions are given.

An application of this method of analysis to the product obtained by the oxidation of phosphorus in moist air at 5° , shows that the solution contains principally hypophosphoric acid. C. H. D.

Apparatus for the Estimation of Carbon Dioxide in Milk. A. BARILLÉ (*J. Pharm. Chim.*, 1909, [vi], 30, 452—453).—The apparatus, which is figured in the original, consists of a flask connected with (1) washbottles containing potassium hydroxide solution through which air freed from carbon dioxide may be introduced at will, and (2) washbottles containing ammoniacal baryta water for the absorption of the carbon dioxide liberated. Eight hundred c.c. of milk are introduced into the flask, heated at 50° , and the last traces of carbon dioxide swept by a current of purified air into the baryta solution, where it is estimated. The "combined" carbon dioxide is then estimated by adding excess of tartaric acid to the milk and proceeding as before. The apparatus gives results within 1% of the theoretical.

T. A. H.

Estimation of Potassium in Potassium Silicates. AART VERWEY (*Zeitsch. anal. Chem.*, 1909, 48, 760—762).—A slight modification of Lawrence Smith's well-known method. One gram of the finely-powdered silicate is intimately mixed with 1 gram of pure ammonium chloride and 5 grams of alkali-free calcium carbonate, and the whole is introduced into a platinum crucible 4.5 cm. in height and 3.5 cm. in width. After covering the mixture with a layer of 3 grams of calcium carbonate, the crucible is heated until the ammonia is expelled, and, after putting the lid on, a strong heat is applied for an hour with a Teclu or a powerful Bunsen burner.

The mass is then boiled with water for fifteen minutes, and, when cold, the liquid is made up to 200 c.c., and in 50 or 100 c.c. of the filtrate the potassium is estimated by acidifying with hydrochloric acid and evaporating with excess of platinic chloride as usual.

L. DE K.

Estimation of Zinc and Analysis of Zinc Ores. K. VOIGT (*Zeitsch. angew. Chem.*, 1909, 22, 2280—2285).—Complete analyses are given of a few zinc ores by known methods. The author prefers precipitating the zinc as zinc ammonium phosphate after removing any calcium with ammonium carbonate in ammoniacal solution. Sulphur is best estimated after a preliminary fusion with a mixture of 1 part of anhydrous sodium carbonate and 3 parts of potassium sulfate. If the ore contains an appreciable amount of matter

insoluble in acid, this should be fused with sodium carbonate and then again treated with hydrochloric acid.

L. DE K.

The Most Rapid Wet Lead Assay. JULIUS F. SACHER (*Chem. Zeit.*, 1909, 33, 1257—1258).—A slight modification of Alexander's process (separation of lead as sulphate, dissolution in ammonium acetate, and titration of the slightly acidified solution with standardised ammonium molybdate with tannin as external indicator).

The author finds the previous separation of the lead as sulphate unnecessary, and titrates the nitric acid solution at once after adding first a sufficiency of ammonia and then an excess of acetic acid.

Supposing 1 c.c. of the molybdate solution = 0.01 gram of lead, a correction must be made depending on the final volume of the liquid. For 50 c.c., 0.18 c.c. of molybdate should be deducted; for 100 c.c., 0.3 c.c.; for 125 c.c., 0.40 c.c.; for 150 c.c., 0.45 c.c.; for 175 c.c., 0.50 c.c.; for 200 c.c., 0.54 c.c.; for 250 c.c., 0.60 c.c.; and for 300 c.c. of liquid, 0.75 c.c. of molybdate solution.

If iron is present to any extent, it should be removed from the solution by heating this for some time on the water-bath.

L. DE K.

Detection of Mercury in Urine. WILH. BECKER (*Pharm. Zeit.*, 1909, 54, 987).—Polemical. A reply to Stich (*Abstr.*, 1909, ii, 1056). The method given by Almén only yields approximate results, but the processes communicated by Farup and by Schumacher-Jung allow the determination of 0.1 mg. of mercury in urine. Bunge's balances, provided with a glass micrometer and indicating 1/20 mg., are recommended.

L. DE K.

Detection of Mercury in Urine. FRITZ GLASER and A. ISENBURG (*Chem. Zeit.*, 1909, 33, 1258).—To 250 c.c. of the sample are added 5 grams of pure aluminium sulphate, and the solution is heated and precipitated with ammonia. The precipitate is then collected, dissolved in hydrochloric acid, and heated on the water-bath for forty-five minutes in presence of a copper spiral. The deposit is then, as usual, sublimed and converted into the red iodide.

L. DE K.

Electro-analysis of Mercury Compounds with a Gold Cathode. F. MOLLWO PERKIN (*Trans. Faraday Soc.*, 1909, 5, 45—48).—Using a gold flag electrode, a large number of estimations of mercury were made, using mercuric chloride, bromide, and sulphate. The electrolytes employed were nitric acid, sulphuric acid, potassium cyanide and sodium sulphide. The results obtained were always high—from 0.5 to 2.5%. This was at first attributed to occluded hydrogen, but it was not found that the gold electrode increased in weight when made the cathode in dilute sulphuric acid and the current passed for twenty hours. When the electrode coated with mercury was treated in a similar manner, it also showed no increase in weight. Since the electrode was cathode, the increase in weight could not be due to oxidation, and when a platinum electrode was run in series with it, the mercury deposited on the platinum was always slightly less than

that theoretically required. The author cannot explain the results, which show, however, that a gold electrode cannot be satisfactorily used for analytical purposes.

A rotating silver electrode showed similar results to the gold electrode. Usually the time required to deposit the mercury was from five to six hours, but on stirring the electrolyte by means of a powerful magnetic field, the time of deposition was reduced to fifty minutes; the results were still too high.

The author comes to the conclusion that the best electrode on which to deposit mercury is one of mercury, the deposition being very rapid if a rotating anode is used (compare Smith and Kolloch, *Abstr.*, 1905, ii, 859; 1906, ii, 194). Two quartz vessels, one of them fitted with a siphon side tube, are described for use with a mercury cathode.

T. S. P.

Estimation of Manganese by Volhard and Wolff's Method. WALDEMAR M. FISCHER (*Zeitsch. anal. Chem.*, 1909, 48, 751—760).—A slight modification of the Volhard-Wolff permanganate titration process. The sulphuric or hydrochloric acid solution (containing about 0.35 gram of manganese) is diluted to 500 c.c., and aqueous sodium hydroxide is added until a slight precipitate forms, which is then at once redissolved by a few drops of dilute sulphuric acid. One gram of freshly ignited zinc oxide and 10 grams of zinc sulphate are added, and, after heating the solution to boiling, it is titrated with $N/10$ permanganate. One c.c. of pure glacial acetic acid is added, and the liquid is again heated to boiling. This causes the precipitate to coagulate and to settle rapidly, and the pink coloration to disappear; the titration is then continued until the pink colour is restored.

L. DE K.

Separation of Manganese and Chromium. FERDINAND FALCO (*Arch. Pharm.*, 1909, 247, 431—436).—A modification of Kassner's process, by means of which good results are obtained when the amount of manganese does not exceed 0.015 gram.

The solution is placed in a covered beaker, and sodium peroxide added in small portions. The liquid is then heated until the precipitate has separated in brown flocks. The liquid is decanted through a filter, and the precipitate washed with boiling water, and finally collected on the filter; the filtrate contains the chromium as chromate. The manganese peroxide is dissolved off the filter by means of hot 20% hydrochloric acid, and returned to the beaker. Excess of bromine water is added, followed by an excess of ammonia, and the liquid is heated to boiling. The precipitate is then collected, washed, ignited, and weighed as manganosomanganic oxide. The filtrate, which may still contain traces of chromium, is added to the main solution.

L. DE K.

Quantitative Separations by Means of Ammonium "Cupferron" (Nitrosophenylhydroxylamine). OSCAR BAUDISCH (*Chem. Zeit.*, 1909, 33, 1298—1300).—*Analysis of Brown Iron Ore.*—Five grams of the ore are dissolved in 60 c.c. of strong hydrochloric acid; the

iron is fully oxidised by boiling with potassium chlorate, and, when cold, the whole is diluted to 500 c.c. Twenty-five c.c. of the liquid are placed in a beaker, and 20 c.c. of hydrochloric acid and 100 c.c. of cold distilled water are added. While stirring, a solution of 3 grams of "cupferron" in 50 c.c. of water is added. The iron is completely precipitated when a white precipitate begins to form. The precipitate is now collected, and washed with cold water until the washings are no longer acid; the filtrate is used for the estimation of manganese. The filter is then washed with dilute ammonia (1:1) to remove the excess of "cupferron," and the precipitate is then washed once with water, and finally converted by ignition into oxide and weighed as such.

Analysis of Nickel Ore.—The iron and copper present are precipitated jointly with "cupferron," and in the filtrate the nickel is estimated by a suitable method. The copper is extracted from the washed precipitate with strong ammonia, and the copper is then obtained as oxide by evaporating the solution and igniting the residue; the oxide may be reduced to metal, and weighed as such. The precipitate insoluble in ammonia is then ignited and weighed as ferric oxide.

The use of "cupferron" in a number of other cases is suggested.

L. DE K.

Rapid Electrolytic Estimation of Cobalt. PIERRE BRUYLANTS (*Bull. Soc. chim. Belg.*, 1909, 23, 383—400).—A lengthy paper containing a large number of experiments recorded in sixteen tables. The electrolytic estimation of cobalt in ammoniacal solution gives good results with a cathodic potential of 1.35 volts. If the same process as for the rapid estimation of nickel is applied, a spongy and partly oxidised metallic deposit is obtained. In any case the metal is very readily oxidised and redissolved, so that it must be washed without interrupting the current. Under proper conditions cobalt may, like lead and manganese, be deposited as peroxide at the anode. Electrolysis from an oxalic acid solution cannot be recommended, as the deposit then contains carbon.

An approximate separation of cobalt from zinc may be obtained when operating in ammoniacal solution as directed above. If sodium sulphite is also added, the cobalt, although free from zinc, contains an appreciable amount of sulphur.

L. DE K.

Gravimetric Estimation of Chromium; Quantitative Hydrolysis of Sesquioxides. WALTER SCHOELLER and WALTER SCHRAUTH (*Chem. Zeit.*, 1909, 33, 1237).—The neutralised solution of the chromic salt, which contains 0.1—0.2 gram of metal, and is diluted to about 300 c.c., is heated to boiling, and 3 c.c. of aniline are added in portions of 1 c.c. After boiling for five minutes, the chromium has been precipitated quantitatively as hydroxide in a form which may be readily washed by decantation.

The process may be used in the presence of manganous salts. Salts of aluminium, zinc, and ferric iron are also precipitated by aniline, but whether the process is sufficiently accurate for these metals has not, as yet, been decided.

L. DE K.

Estimation of Titanic Acid in Ilmenite. ELISE RÖHR (*Chem. Zeit.*, 1909, 33, 1225—1226).—0.5 Gram of the finely-powdered ore is heated with 10 grams of anhydrous sodium carbonate, finally over the blowpipe for half an hour. The liquid mass is poured into a platinum dish placed in cold water, and when cold it is put together with the crucible into a spacious beaker containing 50 c.c. of cold water. The portion left undissolved is washed on a filter, then transferred to an Erlenmeyer flask of one litre capacity, and heated with dilute hydrochloric or sulphuric acid until quite dissolved.

When cold, the solution is rendered slightly alkaline with sodium hydroxide, and then again slightly acidified with sulphuric acid. One hundred c.c. of strong sulphur dioxide solution are added, and enough water to obtain a volume of 700 c.c. The whole is now boiled on an asbestos plate for one hour, and another 20 c.c. of sulphur dioxide solution are added. After remaining for a few hours in a slanting position, the precipitate is collected, washed with boiling water, ignited, and weighed as titanium peroxide. L. DE K.

Estimation of Thorium in Monazite. Colorimetric Estimation of Small Amounts of Platinum. JOHN C. H. MINGATE (*Records Geol. Survey N. S. Wales*, 1909, 8, 276—286).—*Estimation of Thorium in Monazite.*—Samples of Carolina monazite have been analysed by several methods. The precipitate obtained with sodium thiosulphate must be redissolved, precipitated with oxalic acid, and extracted with ammonium oxalate. Precipitation with moist lead carbonate (Giles, *Abstr.*, 1905, ii, 615) gives good results if the precipitation is repeated. Precipitation as basic acetate (Haber, *Abstr.*, 1898, ii, 295) is rapid and sufficiently accurate. Several Australian monazites have also been examined, the richest being a sand from Black Swamp, Torrington, New South Wales, containing 4.12% of thorium.

Colorimetric Estimation of Platinum.—The small quantities of platinum occurring in beach sands or alluvial deposits may be estimated by fluxing with litharge and charcoal to obtain a lead button, cupelling with the addition of silver, and parting with nitric acid, D 1.28, which dissolves platinum and silver, leaving gold and iridosmina. The silver is precipitated as chloride, and the filtrate evaporated twice to dryness with hydrochloric acid. The hydrochloric acid solution, filtered from traces of lead and silver chlorides, is treated with stannous chloride or potassium iodide, and the coloration obtained compared with that of a standard solution containing 0.065 gram platinum per litre. Quantities of platinum as small as 0.06 gram per ton may be estimated in this way. C. H. D.

Methods for the Quantitative Chemical Analysis of Animal Tissues. I. General Principles. WALDEMAR KOCH (*J. Amer. Chem. Soc.*, 1909, 31, 1329—1335).—A discussion of the general principles on which accurate methods of analysis of animal tissues depend and of the manner in which the analytical data should be applied in order to yield results of value to the physiologist. The difficulties attending such work are pointed out. It is suggested that the constituents of the cell may be conveniently arranged in the

following classes: (1) lipoids, including phosphatides, cerebrins, and cholesterol; (2) extractives, such as creatine, taurine, and hypoxanthine; (3) inorganic constituents, represented by the ash; (4) proteins; (5) fats; (6) carbohydrates, namely, glycogen. Very few of the methods at present employed for estimating these various groups are at all satisfactory, and it is therefore considered more useful to study the distribution of the three elements, nitrogen, phosphorus, and sulphur, which are of special interest, as they are involved in somewhat different phases of cell activity. From a physiological standpoint, it is desirable to study the same tissue under different conditions, of which the three most important are: (1) the period of growth or development; (2) conditions of pathological change; and (3) conditions of starvation, the first of these being the most favourable for a study of the chemical transformations in the cell.

As an illustration, analyses are given of (1) a very young brain, (2) an adult brain, and (3) a brain from a case of dementia præcox. The young brain contained a larger quantity of extractives than the adult brain, whilst the latter contained a greater proportion of lipoids. The brain from the case of dementia præcox resembled the normal brain, but contained a smaller quantity of partly oxidised sulphur compounds, soluble in water.

E. G.

Methods for the Quantitative Chemical Analysis of Animal Tissues. II. Collection and Preservation of Material. WALDEMAR KOCH and SIDNEY A. MANN (*J. Amer. Chem. Soc.*, 1909, 31, 1335—1341. Compare preceding abstract).—An account is given of the precautions to be observed in order to obtain uniform and representative samples for analysis, and of the methods of preserving the material. The chief methods of preservation are (1) immersion in alcohol, (2) drying, and (3) the addition of a dehydrating agent, such as sodium sulphate or gypsum. The relative advantages and disadvantages of these three methods are discussed.

E. G.

Methods for the Quantitative Chemical Analysis of Animal Tissues. III. Estimation of the Proximate Constituents. WALDEMAR KOCH and EMMA P. CARR (*J. Amer. Chem. Soc.*, 1909, 31, 1341—1355. Compare preceding abstracts).—Methods are described for effecting the separation and estimation of the six classes of constituents referred to by Koch, and the results of the analysis of a sample of meat by these methods are tabulated.

E. G.

Methods for the Quantitative Chemical Analysis of Animal Tissues. IV. Estimation of the Elements, with Special Reference to Sulphur. WALDEMAR KOCH and FRED. W. UPPSON (*J. Amer. Chem. Soc.*, 1909, 31, 1355—1364. Compare preceding abstracts).—Methods are described for estimating the total sulphur in animal tissues and its distribution in the lipoids, extractives, proteins, and inorganic sulphates. In the lipoids, extractives, and proteins, the sulphur exists in both the oxidized and non-oxidized condition, the former being represented by the ethereal or $R\cdot SO_2\cdot OH$ type, and the

latter by the cystine or R·S·H type. Methods are given for the estimation of the sulphur in each of these states of combination.

The results of a study by these methods of the distribution of sulphur in brains of three different ages are tabulated. The percentage of total sulphur does not show any great variation. The results indicate, however, that the lipid sulphur increases at first with age and decreases later, and the organic sulphur compounds, soluble in water, decrease with age.

E. G.

Volumetric Estimation of Phenol by Lloyd's Method. Tribromophenol Bromide and Hexabromophenoquinone. S. C. J. OLIVIER (*Rec. trav. chim.*, 1909, 28, 354—367).—In the author's experience, Koppeschaar's process for the estimation of phenol does not, as Lloyd states (*Abstr.*, 1905, ii, 209), give inaccurate results, and on the contrary the modified form described by Lloyd (*loc. cit.*) gives results less trustworthy than those given by the original process. In this investigation, the author prepared tribromophenol bromide and hexabromophenoquinone, and records certain new data regarding these substances.

Tribromophenol bromide, when heated in an atmosphere of carbon dioxide, begins to evolve bromine even below 100°, and it is to this decomposition that the different melting points ascribed to this substance are due. Mixed with excess of potassium iodide and hydrochloric acid, the bromide liberates 99·6% of the theoretical quantity of iodine, so that the anomalous results recorded by Lloyd cannot be due, as he suggests, to the formation of this substance in the titration of phenol by Koppeschaar's process.

Hexabromophenoquinone was prepared by Benedikt's process (*Abstr.*, 1879, 717), but could not be obtained crystalline. This substance is not formed when excess of bromine is allowed to react with phenol under the conditions prescribed by Koppeschaar, so that Lloyd's anomalous results with this process are not due to this cause.

In using Koppeschaar's process, the time of action of the bromine on the phenol may be reduced to five minutes if not more than 0·09 gram of phenol is used, and if the solution of sodium bromide and bromine is about 0·8 decinormal. The addition of sodium bromide inhibits the formation of tribromophenol bromide. The end reading is clearer if chloroform is added, as suggested by Lloyd (*loc. cit.*).

T. A. II.

Application of Arsenious Acid in Volumetric Analysis. I. FRANZ M. LITTERSCHEID and J. BORNEMANN (*Zeitsch. angew. Chem.*, 1909, 22, 2423—2427).—*Estimation of Dextrose [in Urine]*.—Fifty c.c. of copper sulphate solution (40·948 grams per litre) are placed in a 200 c.c. measuring flask, 20 c.c. of the usual alkaline tartrate solution are added, and the liquid is heated to boiling. Twenty-five c.c. of the dextrose solution (urine), not exceeding 1% in strength, are added, and the boiling is continued for two minutes. To the hot liquid are then added 50 c.c. of arsenious acid solution (9·9 grams per litre; this is equivalent to the copper solution), and also 30 c.c. of 96% acetic acid. When cold, 7 grams of potassium iodide are added in six to eight

portions. When all the copper, including the reduced oxide, has passed into cuprous iodide, the liquid is diluted to the mark and filtered, the first portion of 10 c.c. being rejected. One hundred c.c. are then nearly neutralised with 20% sodium hydroxide, and, after adding 5 grams of sodium hydrogen carbonate and diluting to 400—500 c.c., the free arsenious acid is titrated with *N*/10-iodine as usual. Or the liquid may be nearly neutralised with pure ammonia and diluted to 400—500 c.c. without addition of hydrogen carbonate. The arsenious acid found is equivalent to the copper reduced by the dextrose. A table is given showing the amount of dextrose corresponding with the c.c. of iodine used. L. DE K.

Simple Distilling Apparatus for the Estimation of Pentosans by Tollens' Method. JOHANN TISCHTSCHENKO (*J. Landw.*, 1909, 57, 229—230).—The usual apparatus consists of a flask fitted with a tap funnel and a Kjeldahl distilling bulb, to which the condenser is attached. This is now simplified by making the funnel and bulb in one piece, the funnel passing down through the middle of the bulb; the double boring of the cock is thus avoided. A sketch is given. N. H. J. M.

[**Estimation of Glycogen.**] KARL GRUBE (*Pflüger's Archiv*, 1909, 130, 322—324). EDUARD PFLÜGER (*ibid.*, 325—327).—Polemical.

Quantitative Estimation of Lactic Acid in Cheese. SHIGEHIRO SUZUKI and EDWIN B. HART (*J. Amer. Chem. Soc.*, 1909, 31, 1364—1367).—In connexion with a study of the chemical changes which take place during the ripening of cheese, it was necessary to find a trustworthy method for estimating lactic acid. Palm's method (Abstr., 1887, 307), depending on the formation of basic lead lactate, $3\text{PbO} \cdot 2\text{C}_3\text{H}_5\text{O}_3$, has been found to be inaccurate. Partheil's method (Abstr., 1903, ii, 189), in which the lactic acid is distilled in a current of superheated steam, when applied to *i*-lactic acid, must not be carried out below 130° , and the distillation must be continued until 750 c.c. of distillate have been collected. This method, however, cannot be used in presence of other acids, such as malic, citric, tartaric, oxalic, or succinic, and is therefore unsuitable for cheese analysis. The usual method of estimating lactic acid by adding dilute sulphuric acid to the cheese, extracting with ether, and afterwards separating the acid in the form of its zinc salt, gives fairly satisfactory results when carefully carried out. E. G.

Estimation of Cinnamic and Benzoic Acids in Mixtures of the Two Acids. ANNE W. K. DE JONG (*Rec. trav. chim.*, 1909, 28, 342—348. Compare Abstr., 1908, ii, 993).—The methods already described, such as those of de Jong (Abstr., 1906, ii, 315) and Scheringa (Abstr., 1907, ii, 823), give good results for the volumetric estimation of these two acids, but are unsuitable in cases where other acids are present, or where the constituents must also be isolated and identified.

In the process now described, cinnamic acid is converted into

dibromophenylpropionic acid, which can be separated quantitatively from benzoic acid and identified.

Preliminary experiments with mixtures of the two acids by (1) fractional crystallisation; (2) extraction by solvents; (3) sublimation, and (4) precipitation of metallic salts, did not give promising results.

The process eventually discovered consists in dissolving the mixture under examination in carbon disulphide and determining, either by titration or weighing, the bromine necessary to convert the cinnamic acid present into dibromophenylpropionic acid. This may then be separated quantitatively from benzoic acid by extracting the latter with carbon tetrachloride or by removing it by sublimation.

T. A. H.

Sodium Phosphotungstate as a Reagent for Uric Acid and other Reducing Substances. CARLO CERVELLO (*Arch. exp. Path. Pharm.*, 1909, 61, 434-437).—The reaction in urine with sodium phosphotungstate described by Richaud and Bidot depends on the presence of uric acid, which reduces the reagent and forms a blue colour. Other reducing substances (dextrose, hydroxylamine, morphine, etc.) give the same reaction. The blue colour which ferrous salts give with the tungstate passes in the presence of atmospheric oxygen into a green and then a red colour, as lower tungsten oxides are formed. Reducing agents produce analogous changes in molybdic salts.

W. D. H.

The Iodine Reaction of Adrenaline. LUDWIG KRAUSS (*Biochem. Zeitsch.*, 1909, 22, 131).—A question of priority. The author claims that the reaction with iodic acid described by Fränkel and Allers (*Abstr.*, 1909, ii, 628) was previously described by himself (*Apoth. Zeit.*, 1908, 701).

W. D. H.

Estimation of Morphine in Opium; Extract of Opium and Tincture of Opium. HEINRICH FRERICHS (*Chem. Zentr.*, 1909, ii, 1499-1500; from *Apoth. Zeit.*, 1909, 24, 592-596).—Helfenberger's process is recommended, using 5 grams of dilute ammonia (17 + 85) and water saturated with ether. A convenient separating funnel for washing the morphine crystals is described. The process is also applicable to the extract and the tincture of opium; the latter should be concentrated to about one-third. Opium may be reduced to a definite morphine content by addition of starch; for the extract, lactose may be used.

L. DE K.

Estimation of Urea in Urine. P. W. GILL, F. G. ALLISON, and HARRY S. GRINDLEY (*J. Amer. Chem. Soc.*, 1909, 31, 1078-1093).—A modification of the hydrolysis method. The resulting solution, after heating the urine with hydrochloric acid in an autoclave, is mixed with an excess of sodium carbonate, and the ammonia formed from the urea is then expelled in a current of air and absorbed in standard acid. Under these conditions, no ammonia is yielded by the products of the hydrolysis of creatinine, uric acid, or hippuric acid. A special aeration apparatus is described.

L. DE K.

Estimation of Urea, Allantoin, and Amino-acids in Urine. DOROTHY E. LINDSAY (*Bio-Chem. J.*, 1909, 4, 448—454).—Nitrogen is estimated by (a) Bohland's method; this gives the nitrogen of amino-acids, hippuric acid, creatinine, allantoin, and urea. Estimation by Folin's method (b) gives the nitrogen of urea, allantoin, and ammonia; estimation by the Mörner-Folin method (c) gives the nitrogen of urea and ammonia. Ammonia and creatinine are estimated separately by Folin's method. The difference between (a) and (b) gives the nitrogen of amino-acids (including hippuric acid) and of creatinine; the difference between (b) and (c) gives the allantoin nitrogen. This combination of methods was found to give good results with artificial mixtures.

W. D. II.

Estimation of Purine Bases in Urine. ERNEST L. KENNAWAY (*J. Physiol.*, 1909, 39, 296—310).—When urine is treated by the Camerer-Arnstein method for the estimation of total purines, uric acid loses ammonia; this loss occurs when the precipitate of silver-magnesium urate is boiled. The purine bases do not undergo this loss. The method is, therefore, only correct when employed for the estimation of purine bases in urine from which the uric acid has been removed.

W. D. H.

Vanillin as a Test for Antipyrine and Kriyogenine; Detection of Antipyrine in Pyramidone. CHARLES PRIMOT (*Chem. Zentr.*, 1909, ii, 479; from *Bull. Sci. Pharmacol.*, 1909, 18, 270).—If a small crystal of antipyrine is moistened with 2 c.c. of a reagent consisting of 1 gram of vanillin, 6 grams of dilute hydrochloric acid (1:1), and 100 grams of 95% alcohol, and the whole evaporated on the water-bath, a dark orange-yellow ring is formed first, and afterwards a similar stain on the bottom of the dish is noticed. The test shows the presence of even 0.00095 mg. of antipyrine. Pyramidone does not give the test, and even 0.005 mg. of antipyrine may thus be detected in 0.1 gram of pyramidone. Kriyogenine gives a distinct greenish-yellow coloration when this test is applied.

J. DE K.

Attempt to Estimate Indoxyl in Urine. L. A. MENNECHET (*Chem. Zentr.*, 1909, ii, 1499; from *Bull. Sci. Pharmacol.*, 1909, 18, 458—460).—The urine is defecated by 10 vol. % of basic lead acetate, and a portion of the filtrate, representing 50 c.c. of the urine, is mixed with an equal volume of pure hydrochloric acid. After shaking for five minutes, 5 c.c. of chloroform are added, and the shaking is continued; if the chloroform remains colourless, 2 to 3 drops of hydrogen peroxide solution are added. The chloroform is drawn off, and the liquid is shaken repeatedly with fresh portions of chloroform. The united chloroform extracts are shaken, first with water containing a few drops of sodium hydroxide and then with water, and the indoxyl is titrated by means of standard hypobromite. The chloroform does not become quite colourless at the end of the titration, but retains a slight lilac colour.

L. DE K.

Cause of the Vanillin Hydrochloric Acid Reaction for Camphor. O. TUNMANN (*Chem. Zentr.*, 1909, ii, 1010; from *Schweiz. Wochechr. Chem. Pharm.*, 1909, 47, 517—519).—The active substance contained in commercial camphor, to which the reaction with vanillin and hydrochloric acid is due, is only an impurity, and is not derived from the oil cells of the camphor tree, but exists in the parenchyma cells. It is probably closely related to the phloroglucotannoids, and it seems to play an important physiological rôle. L. DE K.

A Colour Reaction for Gelatin. R. ED. LIESEGANG (*Zeitsch. Chem. Ind. Kolloide*, 1909, 5, 248).—Mixed aqueous solutions of cupric chloride and excess of tripotassium phosphate give, in the presence of gelatin, a violet coloration instead of the usual whitish-green precipitate. G. S. W.

The Value of Benzidine for the Detection of Minute Traces of Blood. E. J. McWEENEY (*Sci. Proc. Roy. Dubl. Soc.*, 1909, 12, 216—223).—The reagent is made by dissolving a pinch of benzidine in 3—4 c.c. of glacial acetic acid just before use, for the mixture itself turns blue after about a minute, 0.5 c.c. is transferred to a test-tube, and 2 c.c. of 10% hydrogen peroxide are added. To the white, opaque mixture is added the material to be examined for blood, and its presence is denoted by an immediate blue coloration. The material requiring investigation consists nearly always of suspected stains, and may be usually obtained as a fine dust by scraping. Should it be found impracticable to obtain a scraping, the fabric may be treated with a drop of normal saline solution, the stained fibres removed to another slide, and treated between slide and cover-glass with a drop of the reagent, when the presence of blood reveals itself by the brilliant blue coloration of the affected fibre. The mass may then be treated on the slide with a drop of 32% potassium hydroxide, so as to render visible the outlines of the individual red cells.

None of the secretions and excretions hitherto tested by the author (saliva, nasal mucus, urine, etc.) has been found to behave towards benzidine in the same way as blood, but precisely similar results are given by many freshly-cut vegetables and fruits (potato and apple for instance), but these no longer give the reaction when boiled for some time, whereas the reaction given by blood solutions is unimpaired by boiling for ten minutes.

A positive result with the benzidine test should not be looked on as absolutely positive proof of the presence of blood, although if the result is negative the absence of blood may be safely assumed. No regard should be paid to colour changes occurring after the lapse of one minute, and a blank test should be made to make sure that the materials and the test-tubes to be used are satisfactory. L. DE K.

General and Physical Chemistry.

Refraction and Dispersion of Air, Oxygen, Nitrogen, and Hydrogen and their Relations. CLIVE CUTHBERTSON and MAUDE CUTHBERTSON (*Proc. Roy. Soc.*, 1910, 83, A, 151—171).—On account of the discrepancies exhibited by existing data, the authors have redetermined the refractivities of the four gases for the wave-lengths $\lambda = 6563, 5790, 5461$, and 4861 . In all cases it is found that Cauchy's formula, $\mu - 1 = a(1 + b/\lambda^2)$, is inadequate for the expression of the dispersion data, the value of b increasing as the wave-length diminishes. Much better agreement is obtained when a formula of the Sellmeier type is employed to represent the results. The constants involved in the Sellmeier formula are calculated for each of the four gases examined, and also for phosphorus, sulphur, and mercury.

H. M. D.

Refraction and Dispersion of Sulphur Dioxide and Hydrogen Sulphide and their Relation to those of their Constituents. CLIVE CUTHBERTSON and MAUDE CUTHBERTSON (*Proc. Roy. Soc.*, 1910, 83, A, 171—176).—Measurements of the dispersion of sulphur dioxide and hydrogen sulphide are recorded, and the data are expressed in terms of Sellmeier's formula, for which the constants involved are calculated.

The refraction data for sulphur dioxide and hydrogen sulphide are compared with those of the component elements, and it is shown that the refractivity does not follow an additive law. For sulphur dioxide the refractivity is 18%, and for hydrogen sulphide 6%, less than that required by the law of addition. Whereas the number of dispersion electrons in sulphur dioxide appears to be equal to the sum of the dispersion electrons in sulphur and oxygen, this relationship does not hold in the case of hydrogen sulphide.

H. M. D.

Refraction and Dispersion of Neon. CLIVE CUTHBERTSON and MAUDE CUTHBERTSON (*Proc. Roy. Soc.*, 1910, 83, A, 149—151).—The refractive index of neon at 0° and 760 mm. was found to be 1.00006716 for the green mercury line ($\lambda = 5461$). From this and values obtained for the red and blue lines of cadmium, the dispersion has been calculated. Previous measurements having shown that the refractivities of the inert gases are very nearly in the ratio of whole numbers, it was anticipated that the refractivity of neon would be exactly twice as large as that of helium. The experimental value is, however, less than this to the extent of 4%.

H. M. D.

Distribution of the Ultimate Rays in the Spectrum of Different Regions of the Sun. ANTOINE DE GRAMONT (*Compt. rend.*, 1910, 150, 37—40. Compare *Abstr.*, 1908, ii, 645).—This paper contains a tabular statement of the wave-lengths for the
VOL. XXVIII. ii.

ultimate rays of great persistency found in the sun. The fact that metalloids, such as tellurium, phosphorus, arsenic, antimony, and boron, have never been recognised in the sun is probably to be explained by the absorption of their ultimate rays by the terrestrial atmosphere.

The author considers that Lockyer's enhanced lines are not due to dissociation, but that they are ultimate rays, and that their appearance gives some indication as to the proportions in which the elements producing them are present.

W. O. W.

Critical Study of Spectral Series. I. The Alkalies, Hydrogen and Helium. WILLIAM M. HICKS (*Proc. Roy. Soc.*, 1910, 83, A, 226—228*).—The experimental measurements of the spectral lines of the alkali metals, hydrogen and helium, have been analysed with the object of determining the relationships between the wave-length numbers. For any one series of lines, the wave numbers can practically all be represented by a modified Rydberg formula. The relationships between certain constants for the series (lithium, sodium, potassium, rubidium, caesium) are expressible by the integers 1, 2, 4, 5, and 6, and these integers are also involved when the atomic volumes of the respective alkali metals are compared.

H. M. D.

Line Spectrum of Calcium given by the Oxy-acetylene Burner. GUSTAVE A. HEMSALECH and CHARLES DE WATTEVILLE (*Compt. rend.*, 1909, 149, 1112—1115).—Using the method described previously (Abstr., 1908, ii, 336, 445, 547, 745), the authors have investigated the spectrum of calcium in the oxy-acetylene flame. The flame contains a very brilliant blue cone, which shows not only the bands which are obtained with a Bunsen burner, but also a series of supplementary bands which are distributed over the whole length of the spectrum. A full list of wave-lengths and intensities is given.

All the calcium lines do not exist at the base of the flame, but are only formed some distance above the orifice of the burner. Even the strongest lines, although visible, are only very faint at the base of the flame; they become very intense just above the blue cone.

A table is given showing that with flames of different temperatures the number of lines between λ 3900 and λ 5000 increases with increasing temperature. It is also shown that the number of lines given by that portion of the flame which extends to the top of the blue cone decreases with rise in temperature.

T. S. P.

The Yellow, Orange, and Red Regions of the High Temperature Flame Spectrum of Calcium. GUSTAVE A. HEMSALECH and CHARLES DE WATTEVILLE (*Compt. rend.*, 1909, 149, 1369—1372).—The authors compare the less refrangible part of the calcium spectrum obtained by them in the oxy-acetylene flame (preceding abstract) with the spectrum obtained by King (*Astrophys. Journ.*, 29, 190) with the electric furnace. With the exception of the line $\lambda = 6708.18$, which is present in the latter spectrum and not in the former, the characters of the spectra are the same, and the causes which produce them are therefore probably thermal. In order to produce the red lines in the

* and *Phil. Trans.*, 1910, A, 210, 57—111.

calcium spectrum, a high temperature, such as that given with the oxy-acetylene flame, is necessary.

The line $\lambda = 6708.18$, which is present in the spectrum of the electric furnace, is probably due to lithium ($\lambda = 6708.08$). This same line is found in the sun-spot spectrum, and therefore lithium is present in the sun.

T. S. P.

Series Systems in the Spectra of Zinc, Cadmium, and Mercury. T. ROYDS (*Ann. Physik*, 1909, [iv], 30, 1024).—In reference to Paschen's paper (this vol., ii, 3), the author points out that he has already measured the Zeeman effect for certain lines in the spectra of zinc and cadmium. In a magnetic field, the lines 6438.7 (cadmium), 6362.6 (zinc), 5528.7 and 4703.3 (magnesium) appear as symmetrical triplets. The magnetic displacement observed for these lines corresponds with values of e/m in good agreement with the value for cathode rays.

H. M. D.

The Spectrum of Antimony. A. KRETZER (*Zeitsch. wiss. Photograph. Photophysik. Photochem.*, 1910, 8, 45—72).—The spark, arc, and flame spectra of antimony have been investigated. The wave-length measurements of the lines and bands are recorded in detail, and compared with the data of previous observers.

H. M. D.

Absorption Spectrum of Potassium Vapour. P. V. BEVAN (*Phil. Mag.*, 1910, [vi], 19, 195—200).—It has been found that the principal series lines of potassium appear in much greater numbers in the absorption spectrum of potassium vapour than in any form of emission spectrum which has as yet been examined. This result is analogous to that obtained by Wood in the case of sodium vapour.

The method of experiment consisted in heating potassium in a steel tube, the ends of which were closed by quartz plates. A beam of light was passed through the tube, and the emergent beam was examined by means of a quartz spectrograph. In this way the author was able to measure the wave-lengths of the principal lines of potassium up to the line corresponding with $n = 26$ in the Kayser and Runge formula. Hitherto the members of the series up to $n = 11$ have been observed, so that fifteen new lines have been added to the list. The wave-lengths of these range from 2928.0 to 2870.0.

A comparison of the absorption spectra of sodium and potassium vapours shows a close correspondence between them, and this is regarded as evidence that the mechanism involved in the two cases is the same.

H. M. D.

Absorption Spectra of Various Salts in Solution, and the Effect of Temperature on Such Spectra. XXVI. HARRY C. JONES and W. W. STRONG (*Amer. Chem. J.*, 1910, 43, 37—90).—A detailed account is given of an investigation of the absorption spectra of various potassium, uranium, and neodymium compounds by the methods employed by Jones and Uhler (*Abstr.*, 1907, ii, 147, 211, 212) and by Jones and Anderson (*Abstr.*, 1909, ii, 197, 359). The absorption spectra of potassium ferricyanide, ferrocyanide, chromate,

and dichromate, and of uranyl acetate, bromide, chloride, nitrate, and sulphate in aqueous solution, of uranyl acetate, nitrate, and chloride in methyl alcohol, and of uranyl nitrate and chloride in ethyl alcohol are recorded. The effect of dehydrating agents, such as calcium and aluminium chlorides, has been determined. Photographic records have been obtained of the absorption spectra of uranous chloride and sulphate, and the absorption spectra of neodymium chloride in glycerol and in mixtures of glycerol and water have been studied. The effect of changes of temperature of solutions of various salts at different concentrations has been investigated, and spectrograms for a given concentration of a salt have been made at 0° , 15° , 30° , 45° , 60° , 75° , and 90° for a layer of constant thickness.

The absorption spectra of the uranyl salts contain a series of bands in the blue and violet which are usually diffuse. The position of the uranyl bands is not affected by dilution. In methyl and ethyl alcohol, the bands of each particular salt occupy different positions. A new set of fine bands in the green has been discovered in the spectrum of aqueous solutions of uranyl chloride; the presence of a small quantity of aluminium or calcium chloride causes them to disappear.

The absorption spectra of the uranous salts are quite different from those of the uranyl compounds.

The absorption spectrum of neodymium chloride in glycerol differs entirely from that of an aqueous solution.

The intensity of the phosphorescence of the same uranyl salts obtained from different solvents by evaporation is found to vary greatly. Monochromatic stimulation fails to excite phosphorescent bands until the wave-lengths reach the region of the uranyl bands.

The NO_3 group has a great influence on the frequency of the uranyl and uranous absorption bands, and of the uranyl phosphorescent bands.

E. G.

A Relation between Absorption and Phosphorescence.
L. BRÜNINGHAUS (*Compt. rend.*, 1909, 149, 1121--1127).—The absorption and phosphorescence spectra of the rare earths are discontinuous, consisting generally of narrow bands. In the absorption spectra, groups of absorption bands are separated by regions of transparency, whereas in the phosphorescence spectra the regions of emission are separated by dark regions. Taking the spectra of praseodymium, erbium, dysprosium, terbium, and samarium as examples, the author shows: (1) that the mean regions of emission are generally little separated from the mean regions of absorption, and (2) that the regions of emission do not coincide with the regions of absorption, but with the transparent regions (either those between the groups of absorption bands or those outside them). There is thus an alternation between the groups of absorption bands and those of phosphorescence.

The results obtained with compounds of the common elements, such as manganese, chromium, iron, copper, etc., confirm those given above. In general, these substances phosphoresce with a colour which is little different in shade from their colour by reflected or transmitted light. For example, chromium sesquioxide when dissolved in alumina gives

the ruby, which phosphoresces with a red light; when dissolved in lime it is green, and the phosphorescence is green.

It seems as if the light emanates from "phosphorogenic" molecules in the interior of the phosphorescent substance. This light undergoes absorption in the superficial layers, and the radiations observed at the surface are only those for which the "phosphorogenic" substance is relatively transparent.

T. S. P.

Theory of the Law of the Optimum of Phosphorescence
L. BRÜNINGHAUS (*Compt. rend.*, 1909, 149, 1375—1377).—Making use of the ideas put forward in a previous paper (preceding abstract), the author develops a relation connecting the intensity (I) of the radiation comprised between two wave-lengths, λ and $\lambda + d\lambda$, which are very close together, and the concentration (c) of the phosphorogenic substance in a phosphor. The relation is $I = kcs^{-Bc}$, where k and B are constants, B depending on the phosphorescent substance. T. S. P.

Electrolytic Conductivity of Fluorescent Solutions. A. RASSENFOSSE (*Bull. Acad. roy. Belg.*, 1909, 995—1107).—According to the theory of de Heen, the conductivity of a fluorescent solution should depend on the light to which it is exposed. Experiments on solutions of fluorescein and eosin show that the conductivity is a maximum when they are submitted to the action of light which is absorbed by them, green in the case of fluorescein, and yellow in the case of eosin. Blank experiments on solutions of potassium chloride proved that the conductivity does not vary under the action of light of different colours, and also that the observed variation in the case of the fluorescent solutions is not a thermal effect.

T. S. P.

Luminescence of Crystals. ALFREDO POCHETTINO (*Nuovo Cimento*, 1909, [v], 18, 245—300. Compare Abstr., 1905, ii, 430).—The phenomenon of luminescence has been investigated for 227 specimens of crystals representing 78 kinds of minerals. Several methods of exciting luminescence were used; the more important results were obtained with cathode luminescence, but the anodic luminescence, fluorescence, phosphorescence, and thermoluminescence of the crystals were also investigated when they occurred.

In many cases the nature of the luminescence depends upon the method of excitation, thus for distene the ordinary phosphorescence and the cathode luminescence are of different colours, and in the case of calcite the ordinary fluorescence is polarised and the cathode luminescence is not. The nature of the spectra of the cathode luminescence is in many cases independent of the *E.M.F.* applied to the vacuum tube, but the intensity of the luminescence is generally greater the greater the applied *E.M.F.*, provided the crystals undergo no permanent changes under the influence of the rays. There does not appear to be any definite connexion between the luminescence of crystals and their mineralogical relationships; even crystals of the same substance from different sources may show luminescence of different colours, and some specimens of quartz show luminescence whilst others do not.

Many observations have been made on the orientation of the plane of polarisation of the polarised part of the luminescence. The mineral milerite is dichroic, greenocite shows double cathodic luminescence, and the light emitted from the face of crystals of cassiterite parallel to the z axis is totally polarised. With one exception, the luminescence emitted from crystals of the rhombohedral system is not rectilinearly polarised. The greater the exhaustion of the vacuum tube the more completely is the luminescence polarised, and, in general, all causes which tend to diminish the total intensity of the light emitted diminish the degree of polarisation of the light.

The effect of cathode rays on the minerals is discussed. Many minerals become brown under these conditions, and on the face of a crystal directly exposed to the rays a stain made up of differently coloured concentric rings is sometimes observed. On continued exposure to cathode rays, the capacity of a crystal to become luminous by excitation of the rays diminishes, and this diminution may be temporary or permanent. Fewer substances are rendered luminous by anode rays than by cathode rays, and every mineral so far examined which shows anodic luminescence can also be rendered luminous in some other way. In all cases the luminescence due to anode rays is weakest, less durable, and less polarised than that produced by cathode radiation under corresponding conditions.

G. S.

Dependence of the Photo-electric Effect of the Alkali Metals in Polarised Light on the Wave-length. ROBERT PONT (*Ber. Deut. physikal. Ges.*, 1909, 715—722).—Experiments with an alloy of potassium and sodium and ultra-violet radiation of short wave-length show that the photo-electric behaviour of the alkali metals in polarised light is the same as that observed in the case of other metals.

H. M. D.

Theory of the Ripening Process of the Silver Haloids. A. P. H. TRIVELLI (*Zeitsch. wiss. Photochem.*, 1910, 8, 17—24).—As the result of a microscopic examination of ripened silver haloid plates of high sensitiveness, the author concludes that the ripening process is due to the development of definitely recognisable crystalline structure. In consequence of this structural change, the silver haloid is in a condition of strain, and in consequence is less stable than in the unripened condition. The smaller degree of stability is supposed to be the cause of the greater photo-sensitiveness.

H. M. D.

New Determinations of the Radioactivity of the Thermal Waters of Plombières. ANDRÉ BROCHET (*Compt. rend.*, 1910, 150, 145—148).—The author has redetermined the radioactivity of the waters of Plombières (compare Abstr., 1908, ii, 143). The radioactivity of the gases spontaneously liberated from the various waters was measured, and then the latter were agitated with an equal volume of air, and the radioactivity of the latter measured in the apparatus of Chéneveau-Laborde. The tabulated results give the

altitude of the spring, the outflow per twenty-four hours, mean temperatures in 1859—1861, Sept., 1908, and August, 1909, the total solids per litre, the radioactivities in milligram-minutes per 10 litres of the gases and the waters, and the total radioactivity for twenty-four hours.

The waters are strongly radioactive, the radioactivity being due to radium emanation. The total radioactivity of the 22 springs is 74620 milligram-minutes for an average outflow of 67244 cubic metres of water per twenty-four hours. The average radioactivity is 1.11 milligram-minutes per 10 litres, the Lambinet water being the most active (2.18). It is calculated that 55—60 mgms. of radium bromide are contained in the total output of water per minute (507 litres). This quantity is defined as the *radioactive power* of the Plombières waters.
T. S. P.

The Recoil of Radium-*C* from Radium-*B*. WALTER MAKOWER and SIDNEY RUSS (*Phil. Mag.*, 1910, [vi], 19, 100—115. Compare Abstr., 1909, ii, 455).—The active deposit of radium on a platinum plate was mounted opposite a metal disc in an exhausted tube for some minutes, so that the disintegration products recoiling from the plate would be received on the disc. The plate was first freed from adhering emanation and from radium-*A* by heating at 360° in a vacuum for half an hour before use. It was found that, in general, both radium-*B* and -*C* were radiated to the disc, but if three hours elapsed between the preparation of the active deposit and the recoil experiment, only radium-*C* was obtained. They consider that the radiation of radium-*C* may not in all cases be a primary recoil effect, but due to mechanical disturbance produced by the recoil of radium-*D*. The amount of radium-*C* recoiled varies with the same plate with the time in an unexplained manner, and is always small compared with the amount of radium-*B* recoiled. Since radium-*B* gives only a β -particle, it is to be expected that radium-*C* will recoil with far less energy than radium-*B*, which results from the recoil of the α -ray-expelling radium-*A*. But the energy of the recoiling radium-*B* atom is apparently far greater than theory would indicate. Its power of penetrating air is about 1/40th of that of recoiling radium-*B*. Attempts to detect an electric charge on the recoiling radium-*C* atom have failed (compare Makower, Abstr., 1909, ii, 456; *Le Radium*, 1909, 6, 50).
F. S.

Disengagement of Emanation from Radium Salts. L. KOLOWRAT (*Le Radium*, 1909, 6, 321. Compare Abstr., 1907, ii, 729).—The paper is devoted to a detailed reconsideration of many of the points previously discussed. The anomaly encountered, in that the disengagement of emanation from radiferous barium chloride decreases with rise of temperature from 830° to a minimum at 920°, and then increases again quickly to the m. p. at about 950°, is probably explained by Plato's observation of the existence of two forms of barium chloride with transformation point 34.4° below the m. p. (Abstr., 1907, ii, 239). Similar behaviour of barium fluoride indicates a similar polymorphic transformation between 1000° and 1100°.

Additional salts studied comprise potassium nitrate, silver chloride, and caesium nitrate. Nineteen series of experiments have been made on the growth with time of the amount of emanation retained by the salts at varying temperatures, after complete initial removal of the emanation by fusion, both when the temperature is maintained and also when during part of the time the salt is not heated. The results are interpreted on the view that a definite temperature, different for different molecules, exists for each molecule of emanation formed within the salt, below which it is retained. The amount of emanation retained at any temperature is the sum of all the molecules the temperatures of disengagement of which are above that temperature. No evidence of any want of homogeneity of the emanation disengaged at different temperatures was obtained (compare Rutherford, Abstr., 1909, ii, 457; Debierne, *ibid.*, 534). F. S.

Nature of the Ionisation of a Molecule by an α -Particle. R. D. KLEEMAN (*Proc. Roy. Soc.*, 1910, 83, A, 195—199).—If the energy of ionisation is derived from the kinetic energy of the α -particle, the electrons ejected from molecules should on the whole possess a motion in the direction of the α -particles. In the experiment designed to test this, α -particles from a plate covered with polonium were passed through a very thin aluminium foil, and fell on a parallel aluminium plate in hydrogen and also in air at a low pressure. If the emergent electrons from the foil are more numerous than the incident electrons from the plate, when an electric field is applied between the foil and plate, the current should be larger with the foil negative than vice versa, and this difference should be the more marked as the potentials are increased. Experiments in hydrogen at 0.8 mm. pressure show a well marked difference, increasing rapidly as the voltage is increased above the point at which the expelled electrons acquire sufficient velocity to ionise by collision. The experiments support the view that the energy of ionisation is derived from the ionising agency, not by "trigger" action, from an internal store in the molecule ionised. F. S.

The Number of α -Particles Expelled from the Actinium and Thorium Emanations. H. GEIGER and E. MARSDEN (*Physikal. Zeitsch.*, 1910, 11, 7—11. Compare Bronson, Abstr., 1908, ii, 792).—By a further development of the method of counting α -particles by the scintillations produced in zinc sulphide, interesting confirmation and extension have been obtained of Bronson's conclusion that the thorium emanation must give at least four α -particles and the actinium emanation at least two α -particles on disintegration. The number of scintillations produced by the emanation and active deposit together in equilibrium and by the active deposit alone, after the supply of emanation has been stopped and the emanation allowed to decay, is as 3 to 1 both for thorium and actinium, showing that the emanation produces twice the number of α -particles produced by the active deposit. The thorium active deposit is known to produce two α -particles. [A similar conclusion in the case of the actinium active deposit (compare Blanquies, Abstr., 1909, ii, 634) is not referred to.]

Emanation was allowed to diffuse between two parallel zinc sulphide screens placed close together, film side inwards, and the number of scintillations on exactly opposite portions of the two screens counted simultaneously by two observers with two microscopes. For actinium emanation a very large proportion of the scintillations, up to 66%, occurred in pairs, showing that two particles are expelled simultaneously or at least with less than 0.1 second between them. With radium emanation and active deposit in equilibrium, only 2 to 4% of pairs was observed. For thorium emanation it was established that the four α -particles expelled were not simultaneous. A large number of cases of successive scintillations in similar parts of the field were observed, with a time interval between the two scintillations from half a second to an unmeasurably short time. This occurred even when extremely few scintillations were produced. The existence of at least one short-lived α -ray product in the thorium series, with a period of average life of about 0.2 second, is indicated, but full elucidation of this case is not yet arrived at. F. S.

The Absorption of Cathode Rays of Different Velocity in Helium. JAMES ROBINSON (*Physikal. Zeitsch.*, 1910, 11, 11—13).—The cathode rays obtained by the action of ultra-violet light on a negatively charged plate were employed. The velocity of the rays was varied by varying the charge on the plate. With decreasing velocity of cathode rays the absorption by gases attains a maximum. In hydrogen the maximum is reached more suddenly and at lower velocity than in other gases. In helium, the absorption with decreasing velocity increases at first only very slowly down to far smaller velocities than for other gases. The absorption then rises with great abruptness to the maximum. Helium thus resembles hydrogen, but the peculiarities shown by the latter gas are even more marked in helium. F. S.

Contact Electrification. ALBERT GRUMBACH (*Compt. rend.*, 1909, 149, 846—848. Compare Gouy, Abstr., 1906, ii, 652).—According to Helmholtz the contact potential of a liquid with glass is proportional to $\rho P/\eta E$, where E is the *E.M.F.* acquired by the liquid of viscosity η and resistivity ρ in passing through a glass capillary tube under pressure P .

The author finds that in a $N/1000$ -solution of potassium chloride in water E , is strictly proportional to P . The addition of 5.6% of phenol to the solution increases the viscosity η in the ratio 1:1.09, but does not alter the conductivity. The capillary *E.M.F.*, however, undergoes a marked reduction. In two series of experiments the addition of phenol altered the contact potential in the ratios 1:0.80 and 1:0.78 respectively. R. J. C.

Dielectric Properties of the Elements. DIMITRI K. DOBROSERDOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1164—1171).—As usually determined, the dielectric capacity K refers to large wave-lengths, and the index of refraction, n , to very small wave-lengths, and, in order to test Maxwell's law, $n^2 = K$, it is necessary to obtain values of n and K referring to comparable conditions. The value n_∞ of n for very large

wave-lengths may be calculated by means of Cauchy's formula, $n = A + B\lambda^{-2} + C\lambda^{-4}$, where $n_{\infty} = A$. But this process of extrapolation gives results agreeing with the experimental values only when λ varies within narrow limits, so that the values of n_{∞} thus obtained must necessarily be somewhat inaccurate, and it is found that n_{∞}^2 and K have identical values only in exceptional cases.

A list is given of the values of n_{∞}^2 and K for such elements as have been previously investigated, and in all cases the differences between the two are considerably less than those observed for complex liquids and solids. These results confirm Schmidt's view (*Ann. Physik*, 1902, [iv], 9, 919) that, in the elements, the molecules have an especially simple structure.

The dielectric constants of the non-metals increase with the valency in any horizontal row of the periodic system and with the atomic weight in any vertical column. For helium, $n = 1.0000375$ or $n^2 = 1.000075$, whilst K has the value 1.000074. For the other rare gases of the atmosphere, the calculated values of K (n^2) show a continuous increase with the atomic weight. Determinations of the dielectric constants of the metals are insufficient in number to allow of any similar regularity being observed.

T. H. P.

Quantitative Relations between the Dielectric Constants and other Properties of Substances. DMITRI K. DONROSEDOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1385—1406).—The author has investigated the validity of various relations between the dielectric constant and other physical constants which have been suggested by various investigators. It was shown by Obach (*Abstr.*, 1892, 158) that for the members of certain homologous series of organic compounds, proportionality exists between the dielectric constant and the latent heat of evaporation, or $\rho/K = \text{const.}$, the actual magnitude of the ratio being different for different series. The author has calculated the value of the ratio for organic compounds belonging to nine homologous series, the mean and limiting values found being as follows: (1) propionic esters, 15.20 (14.84—15.39); (2) butyric esters, 15.41 (15.04—15.78); (3) valeric esters, 15.56 (15.03—16.27); (4) ketones, 6.00 (4.95—7.1); (5) alkyl derivatives of benzene, 31.0 (29.73—33.02); (6) aliphatic acids, 39.55 (39.06—40.05); (7) nitriles, 5.65 (4.7—7.31); (8) amines, 25.47 (25.0—26.0); (9) alkyl halogen compounds, 6.61 (6.32—6.95). The values obtained by Obach were: (10) formic esters, 11.85 (11.03—12.78); (11) acetic esters, 13.72 (13.26—14.20); (12) ethyl esters of fatty acids, 13.34 (11.15—14.20); (13) monohydric alcohols and water, 7.41 (6.22—7.91), the values for isopropyl (6.14) and cetyl (9.1) alcohols being of doubtful accuracy. The mean of the values obtained for groups (13), (7), (4), and (9) is 6.46; for groups (10), (11), (1), (2), (3), and (12), 14.18; for group (8), 25.47; for group (5), 31, and for group (6), 39.55, these numbers, 6.46, 14.18, 25.47, 31, and 39.55, being approximately in the ratios of 1, 2, 4, 5, and 6. When all the other compounds (inorganic as well) for which the values of ρ and K are known are included, the values of the constant have the approximate proportionate magnitudes: 0.5 : 1 : 2 : 3 : 4 : 5 : 6. The chemical nature of any particular compound

seems to have no appreciable influence in determining to which group it belongs, members of one group being compounds completely different as regards their chemical characters.

The relationship between dielectric constant and chemical constitution of a dielectric given by Thwing (Abstr., 1894, ii, 374), and expressed by the equation: $K = d(a_1K_1 + a_2K_2 + \dots)/M$ (where d is the density, and M the molecular weight of the compound, a_1, a_2, \dots the atoms or atomic groups of the same kind composing the molecule, and K_1, K_2, \dots the dielectric constants of the atoms or groups), is not confirmed by the experimental numbers collected by the author.

The relation discovered by Lang (Abstr., 1896, ii, 144) for gases, namely, $(K-1)10^6/S = \text{const.} = 123(116-145)$ (S being the sum of the valencies of the atoms constituting the molecule of the gas), holds only, as far as can be ascertained, at 0° and 760 mm. pressure for the six gases obeying Maxwell's law, $K = n^2$.
T. H. P.

The Conductivity of Mixtures of Dilute Solutions. J. A. GARDINER (*Trans. Roy. Soc. Canada*, 1908, [iii], 2, iii, 37-52).—Barton has recently shown that a fall in the conductivity of the solution occurs when dilute hydrochloric acid is added to a colloidal solution of silver or to a dilute solution of silver nitrate. If the ordinary law of electrolysis were followed, a rise in the conductivity should occur.

The author's experiments show that as a $N/10,000$ solution of hydrogen chloride is added to water, there is, at first, very little change in the conductivity of the solution, but as the acid solution becomes more concentrated, the conductivity gradually increases. On the addition of hydrochloric acid to silver nitrate of various dilutions, a drop in the conductivity was observed. When, however, a 39.5×10^{-7} normal silver nitrate solution was reached, this effect disappeared. A similar drop in the conductivity was observed when a dilute nitric acid solution was added to a dilute silver chloride solution. The conductivity of a silver nitrate solution steadily increased with the concentration.

It is suggested that the abnormalities here recorded may be due to: (1) the absorption of hydrogen by the platinum electrodes; (2) the hydrogen ion attracting to itself the neutral silver chloride, and becoming loaded so that its mobility falls below that of the silver ion which it displaces.
E. J. R.

Cadmium Chloride Concentration Cells. EUGEN VON BRON and B. P. APHANASSIEFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1175-1182).—The authors have measured the *E.M.F.* of cadmium chloride concentration cells with and without transport of the cation. In the first case, silver chloride electrodes prepared by Jahn's method were used, and one of the solutions had the same concentration and the other different concentrations for the different cells. The curve connecting the log. of the number of grams of salt per 1 gram of water in the variable solution with the *E.M.F.*, calculated for 1 equivalent of salt per litre in the constant solution, exhibits a spread-out maximum for solutions containing 6-8 equivalents of salt. This maximum corresponds with solutions in which the transport

number of the cation is zero. A line drawn parallel to the axis of log. concentrations cuts the curve in two concentrations, which would give a cell having a zero *E.M.F.*, although diffusion would occur. If the concentrations of the two solutions are below the maximum point on the curve, the positive electricity is directed from the more concentrated to the more dilute solution; that is, with the diffusion current, whilst if the concentrations are greater than the maximum, the reverse is the case.

With cells without transport, the curve connecting *E.M.F.* and log. of the concentration is approximately linear for solutions containing 1—3 equivalents of cadmium chloride, but for higher concentrations it becomes more complex. The curve does not, however, show any of the peculiar bends observed by Godlewski (*Abstr.*, 1902, ii, 445), whose observations are inaccurate, owing to irreversible processes at the electrodes of which he took no account.

The transport numbers for the anion and cation are calculated, the values for the former agreeing well with those obtained by Hittorf's method (compare *Abstr.*, 1908, ii, 145, 250). Concentration cells with concentrated solutions hence show the same diffusion phenomena as are observed in those with dilute solutions, and Nernst's theory of diffusion of electrolytes is justified as well for concentrated as for dilute solutions (*loc. cit.*). T. H. P.

Rapid Formation of Positive Lead Accumulator Plates. GERHARD JUST, PAUL ASKENASY, and B. MITROPANOFF (*Zeitsch. Elektrochem.*, 1909, 15, 872—892).—The effect of repeatedly charging and discharging lead plates immersed in sulphuric acid and in mixtures of sulphuric and nitric acids is investigated. In presence of nitric acid the attack on the plates is much more rapid, lead sulphate being first formed. This is subsequently oxidised to lead peroxide. With smooth plates, however, it appears to be impossible to obtain a sufficiently adherent coating of lead peroxide; with plates built up of a large number of small lead sheets, so as to give a large surface, good results were obtained. In the solutions containing nitric acid, lead nitrate is formed at the anode, and this is converted into lead sulphate at some distance from the surface of the plate. This distance increases as the concentration of the nitric acid increases and that of the sulphuric acid diminishes. When it is sufficiently small, an adherent deposit is obtained; when it is greater a loose deposit is formed, and when it is greater still, a precipitate of lead sulphate is produced in the solution. A solution containing 30 grams of potassium nitrate and 218 grams of sulphuric acid per litre appears to give the best results. T. E.

Volatilisation of Cathodes. VI. VOLKMAR KOHLSCHÜTTER (*Zeitsch. Elektrochem.*, 1909, 15, 930—937).—In reply to the criticism of Starck and Fischer (*Abstr.*, 1909, ii, 718), the author says that between the value of the cathode fall of potential at which volatilisation begins and the higher value at which it ceases to increase proportionally to the cathode fall, the volatilisation is quite a definite reproducible quantity; the relation of the quantity volatilised

to the atomic weight of the metal is too striking to be regarded as accidental. He inclines to regard Starck's theory of the phenomena as a distinct advance.

New experiments with gold and platinum in oxygen and with platinum in air are described. Satisfactory measurements could not be made in these gases with other metals, because they react with the gas in circumstances which cannot be controlled. The chemical reaction causes the discharge to become intermittent, which is indicated by a telephone in the circuit. In oxygen the regular volatilisation is observed between 440 and 1200 volts cathode fall for gold and between 500 and 900 volts for platinum. T. E.

Electrode for Determining the Concentration of the CO_3^{2-} Ion and the Condition of Silver Carbonate in Solution. JAMES F. SPENCE and MARGARET LE PLA (*Zeitsch. anorg. Chem.*, 1909, 65, 10—15).—Pure silver carbonate is best prepared by adding a dilute solution of sodium hydrogen carbonate to a concentrated solution of silver nitrate, stirring continuously. A silvered platinum wire, covered with the freshly precipitated carbonate, has a constant potential. With pure sodium carbonate solution as the electrolyte, the value $\text{Ag} \cdot \text{Ag}_2\text{CO}_3 \cdot N/1\text{-CO}_3^{2-} = +0.7545$ volt is found, and the concentration of the CO_3^{2-} ion, c' , is found in any solution by the relation $\epsilon = 0.7545 - 0.029 \cdot \log. c'$. The solubility of silver carbonate in water at 25° is thus found to be 1.16×10^{-7} mol. per litre (compare Abegg and Cox, *Abstr.*, 1904, ii, 256), and the salt is almost completely hydrolysed.

C. H. D.

Investigation of Electrolysis with the Ultramicroscope. J. J. KOSSONOGOFF (*Physikal. Zeitsch.*, 1909, 10, 976—986).—An arrangement is described by means of which the author has applied the ultramicroscope to the examination of solutions through which an electric current is passed. When a current is started through a solution of silver nitrate or copper sulphate, a very considerable increase in the number of bright points in the field of view of the ultramicroscope is at once observed. The view is put forward that these are associated with the ionic carriers of the electric current. In support of this it is found that ultramicroscopic effects of a special kind are observed when the potential difference between the electrodes is raised to that which corresponds with the tension of decomposition. In the case of the above-mentioned solutions, the attainment of the critical potential difference is accompanied by a very special distribution of the bright points in the neighbourhood of the cathode. At a short distance from this electrode, and parallel to it, a zone can be distinguished in which the bright points are very closely crowded together. Between this special zone and the electrode itself is a region which is almost entirely free from bright points. This is supposed to correspond with the dark cathode space in gaseous discharge. The appearance of this effect at a particular voltage affords an optical method of determining decomposition tensions.

Similar effects have also been observed at the anode in other cases.

H. M. D.

Electrolytic Oxidation of Ammonium Carbonate. FRITZ FICHTER and HANS KAPPELER (*Zeitsch. Elektrochem.*, 1909, 15, 937—943. Compare Brochet and Boiteau, *Abstr.*, 1909, ii, 657).—A solution of ammonium carbonate containing 3.669 gram-molecules of ammonia and 2.494 molecules of carbon dioxide per litre was electrolysed between platinum electrodes at temperatures from 20° to 60° and with anodic current densities between 0.027 and 0.731 amperes per sq. cm. Ammonium nitrate is the principal product; neither carbamide nor nitrite could be detected. The experiments were always stopped when a comparatively small quantity of the ammonium carbonate was oxidised. The gases evolved contained carbon dioxide, ammonia, oxygen, and hydrogen; nitrogen was not found. In an open vessel the yield increases with the current density and with the temperature. In a closed vessel, however, very much worse yields were obtained; this is due to the fact that in an open vessel the solution loses ammonium carbonate rapidly, and dilute solutions give better yields than more concentrated ones. The best results were finally obtained with a current density of 0.4 to 0.6 ampere per sq. cm., a temperature of 50—60°, and a solution containing about 2 mols. of ammonia per litre, the ratio CO_2/NH_3 being 0.27; in these circumstances the current efficiency is from 82% to 97%. A solution of ammonium tetraborate gives very similar results. T. E.

Electro-catalysis. D. ALEXÉEFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1155—1160).—By the electrolysis of ammonium sulphate with lead peroxide electrodes, nitrogen, oxygen, and nitrous oxide are evolved, but neither nitrite nor nitrate is formed in the solution. Hence the oxidation of the ammonia does not proceed further than the stage $\text{NH}(\text{OH})_2$, the anhydride of which is nitrous oxide, hydroxylamine forming an intermediate oxidation product. The evolution of nitrogen occurs according to the equation: $\text{NH}_2\text{OH} + \text{NH}(\text{OH})_2 = \text{N}_2 + 3\text{H}_2\text{O}$. That the nitrogen and nitrous oxide developed do not arise by the formation and subsequent decomposition of ammonium nitrite and nitrate is shown by experiments on the oxidation of hydroxylamine (*vide infra*).

With solutions of ammonium sulphate containing sulphuric acid, electrolysis with lead peroxide electrodes yields only nitrous oxide and oxygen, whilst if the ammonium sulphate solution contains ammonia, pure nitrogen is obtained. In the latter case, the formation of NH_2OH predominates over that of $(\text{NOH})_2$, the reaction $2\text{NH}_2\text{OH} + (\text{NOH})_2 \rightarrow 2\text{N}_2 + 4\text{H}_2\text{O}$ occurring in preference to $(\text{NOH})_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$.

The reaction between lead peroxide and hydroxylamine proceeds according to one or the other of the two equations: $2\text{NH}_2\text{OH} + \text{PbO}_2 = \text{PbO} + \text{N}_2 + 3\text{H}_2\text{O}$ and $2\text{NH}_2\text{OH} + 2\text{PbO}_2 = 2\text{PbO} + \text{N}_2\text{O} + 3\text{H}_2\text{O}$, according to whether the hydroxylamine or the peroxide is in excess. In practice, as is shown by a study of the products obtained when the reaction takes place in absence of air, a mixture of the two gases is always obtained; the amounts actually formed in two cases were: (1) 22% N_2O and 78% N_2 , and (2) 30% N_2O and 70% N_2 .

Thus, lead peroxide is a typical catalyst, with the peculiarity that

one-half of its action is a chemical and the other a physical process. The formation of nitrogen and nitrous oxide at lead peroxide electrodes is hence a typical electro-catalytic process.

T. H. P

Manganese, Aluminium, and Copper. FRIEDRICH HEUSLER and FRANZ RICHARZ (*Zeitsch. anorg. Chem.*, 1909, 65, 110—112. Compare Ross and Gray, Abstr., 1909, ii, 859).—The fact that certain manganese-aluminium bronzes, heated above 200° and slowly cooled, become strongly magnetic, but have considerable hysteresis, has been observed previously by Heusler and by Asteroth.

C. H. D.

Magnetic Dichroism of Siderite in Liquids. GEORGES MESLIN (*Compt. rend.*, 1909, 149, 855—857. Compare Abstr., 1909, ii, 529).—Siderite, suspended in carbon disulphide or aniline, exhibits magnetic dichroism to such a high degree that the phenomena can be seen with an ordinary permanent magnet or the residual magnetism of an electromagnet. The suspensions are also slightly dichroic spontaneously.

A method of demonstrating dichroism by the optical lantern is described.

R. J. C.

Magnetism of Solutions. PAUL DRAPIER (*J. Chim. Phys.*, 1909, 7, 385—404. Compare Pascal, Abstr., 1908, ii, 927).—The author has examined the behaviour of a number of solutions when placed in a flat, vertical cell between the pointed poles of a powerful electromagnet. If the liquid has paramagnetic properties, it tends to move radially in a plane perpendicular to the lines of force, and thus forms a tumulus or convexity at the surface. This convexity is much accentuated in aqueous solutions when the surface-tension is lowered by adding a layer of ether or benzene.

An aqueous solution of ferric alum or ferric chloride shows a convexity even when only 1% of ferric salt is present, but a solution of the same concentration in ether is unaffected.

Ferric ammonium oxalate is but slightly affected, and colloidal ferric hydroxide, potassium ferrocyanide, and potassium ferricyanide are unaffected.

If a solution of ferric chloride in ether is floated on water, a striated layer is produced, which, in the field, bends downwards into the water, the striae being displaced horizontally. Displacements are also observable if precipitated ferric hydroxide or air bubbles are suspended in the paramagnetic fluid.

Dilute manganese sulphate gives a marked convexity, but potassium permanganate none. When ether is poured on the latter solution an intermediate layer is formed, containing ether, water, manganese sulphate, and precipitated manganese dioxide, which is extremely sensitive to the magnetic field, owing to manganese sulphate and, perhaps, to free oxygen occluded in the precipitate.

Cobalt and nickel hydroxides precipitated by ammonia are also very sensitive to the magnetic field.

Chromium sulphate, cobaltous chloride, and nickel nitrate are

paramagnetic; potassium dichromate, potassium cobalticyanide, titanium sulphate, and platinum chloride are not.

The author's observations confirm the conclusion arrived at by Pascal by a different method, that as a magnetic metal becomes more and more removed from its normal (ionised) state, it loses its paramagnetism.

The magnetic capillary rise of solutions of ferric alum and ferric chloride of 5, 7½, and 10% strengths was investigated. On increasing and decreasing the exciting currents between 0 and 10 amperes, marked hysteresis was found in the capillary rise, apart from the usual hysteresis of the magnet. This effect is supposed by the author to be true liquid hysteresis.

R. J. C.

Use of the Magnetic Field as a means of Determining Constitution in Organic Chemistry. II. and III. PAUL PASCAL (*Bull. Soc. chim.*, 1909, [iv], 5, 1110—1118; 1910, 7, 17—28. Compare Abstr., 1909, ii, 487, 788, 859).—Part of this work has been published already. From comparisons of the magnetic susceptibility of oxygen in a series of oxygenated carbon compounds, the conclusion is drawn that the value is -48×10^{-7} where oxygen is joined to two different carbon atoms, -35×10^{-7} where it is doubly linked to a carbon atom, the latter being itself joined to two oxygen atoms (as in carboxylic acids), and $+18 \times 10^{-7}$ where a single oxygen atom is doubly linked to carbon (as in aldehydes and ketones). A comparative list of (1) experimental, molecular, magnetic susceptibilities, and of (2) values calculated from the data given above, shows close concordance. The application of these rules to the case of paraldehyde lends support to the Kekulé formula for this substance.

Apart from the above effect due to the method of linking of oxygen, the value of the magnetic susceptibility of the latter is also influenced by the general structure of the rest of the molecule, and especially by the presence of (1) tertiary or quaternary carbon atoms, (2) double linkings. The first of these effects is marked when the disturbing atom is in position α or γ , and more so in positions δ and ϵ , but is very small in β , ζ , or η , and ceases beyond position θ . The presence of a double linkage shows itself in an analogous manner, and a table of corrections for the effect of double linkings in several positions is given.

The second group of conclusions lends support to Bayer's strain hypothesis, provided the carbon chain is regarded as having a roughly spiral form.

The influence of the hexamethylene nucleus on the magnetic susceptibility is estimated at $+31 \times 10^{-7}$, and with this correction the calculated value for cineol, according to Brühl and Wallach's formula, agrees with that determined experimentally.

Sulphur has the value -156×10^{-7} , and retains this in most of its organic derivatives, but in thioacetic acid the atomic susceptibility of the oxygen atom is -15×10^{-7} , as against -35×10^{-7} for the same oxygen atom in acetic acid, the greater effect in the former case being due to the presence of the sulphur atom.

The normal value for nitrogen is -58×10^{-7} , but in a cyanogen group,

or where nitrogen is directly attached to a benzeno nucleus, the value becomes -48×10^{-7} . In closed chains containing carbon and nitrogen, the latter has the same value as in aromatic amines, and for purposes of calculation, the value for one CH_3 (or CH) group is replaced by that for NH (or N), with the usual total correction for the influence of the nucleus. This rule is not applicable in the case of pyridine.

T. A. H.

Thermometers as Thermo-regulators. ERHARD GLASER (*Biochem. Zeitsch.*, 1909, 23, 5—9).—Into the thermometer which is used as thermo-regulator, platinum wires are fused at certain definite points corresponding with temperatures the constancy of which it is desired to maintain. The lowest platinum wire is always in contact with the mercury when the thermometer is immersed in the apparatus, the temperature of which is to be regulated. By means of this and another platinum wire, corresponding with the temperature which is to be maintained in the thermostat, an electric circuit is made with a coil, in which is immersed a Hahn regulator. As soon as the mercury reaches the higher point and the circuit is closed, an iron core in the Hahn regulator is drawn down by the current and shuts off the supply of gas to the burner heating the thermostat. As the latter cools, the gas is automatically lighted again by means of a by-pass. The apparatus is figured in the paper.

S. B. S.

Krafft's Boiling-point Estimations and his Theory of Volatilisation. C. VON RECHENBERG (*J. pr. Chem.*, 1909, [ii], 80, 547—555. Compare Abstr., 1909, ii, 544).—Largely polemical in reply to Krafft (Abstr., 1909, ii, 969, and Hansen, *ibid.*, 969). It is pointed out that the expression used by Krafft, b. p./0 mm., is a contradiction, as if sufficient vapour is present for the temperature to be determined there must be a vapour pressure. The effects which are attributed by Krafft to the influence of gravity are regarded by the author as due to the condensation of vapour by external cooling.

J. J. S.

Preparation of a Mixture of Constant Boiling-point and Maximum Vapour Pressure by Distillation. D. D. GADASKIN and A. E. MAKOVETZKI (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1160—1163).—The authors describe experiments on the distillation of various aqueous solutions of the ether of methylene glycol under ordinary and reduced pressure (compare Abstr., 1908, i, 753; 1909, ii, 215). The results obtained are discussed by Makovetzki (see following extract).

T. H. P.

Determination of the Composition of Constant Boiling-point Mixtures having Maximum Vapour Pressures and their Quantitative Separation by Distillation. A. E. MAKOVETZKI (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1171—1175. Compare preceding abstract).—The author adduces further evidence in support of his view that a binary liquid mixture, for which a maximum or minimum vapour pressure exists, may be regarded as consisting of two components, one

being the mixture of maximal or minimal vapour pressure, and the other the component present in excess. By means of aqueous solutions of the ether of ethylene glycol, it is shown that the mixture of maximum vapour pressure can be separated quantitatively by one distillation in a suitable fractionating apparatus. The quantity and composition of the mixture with maximum vapour pressure are not altered by the addition to the solution of a non-volatile substance which effects the separation of the liquid into layers, but does not give a solid phase.

T. H. P.

An Electrical Apparatus for the Direct Determination of the Water Value of a Calorimeter. W. ŚWIĘTOSŁAWSKI (*Bull. Acad. Sci. Cracow*, 1909, 548—555).—The principle of the method consists in using two calorimeters, which are heated by means of an electric current. The one calorimeter (chief calorimeter) is filled with the solution the water value of which is required, and the other (water calorimeter) with water. The heating is accomplished by means of a platinum wire spiral, which is fused in between two concentric layers of glass. The two vessels are of the same construction. The heat coefficient α is calculated from the formula:

$$\alpha = \Delta T_1(500 + c_1 + c_1') / \Delta T_2(500 + c_2 + c_2'),$$

where ΔT_1 and ΔT_2 denote the increases in temperature, c_1 and c_2 the water values of the calorimeter with stirrer and thermometer, c_1' and c_2' the water values of the heating apparatus, and where each calorimeter contains 500 grams of water.

The sp. heat K of any liquid can then be calculated from the equation $K = \alpha \Delta T_2 / \Delta T_1$, where the increases in temperature of the two calorimeters are ΔT_1 and ΔT_2 .

J. J. S.

Atomic Volume of Allotropic Modifications at Very Low Temperatures. ERNST COHEN and J. OLIE, jun.* (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 437—445).—In order to obtain information relating to the densities of allotropic modifications at absolute zero, measurements of the densities of diamond and graphite and of white and grey tin were made at a series of temperatures by a dilatometric method. The graphite was subjected to pressures of 1000 to 5000 atmospheres until the sp. gr. remained constant after repeated compression. The ratios of the specific gravities of diamond and graphite were found to be 1.585, 1.583, and 1.582 at 18°, -38°, and -164° respectively; those of white and grey tin, 1.266 and 1.274 at 78° and -164°. These numbers indicate that the specific volumes of the allotropic forms do not converge as the temperature falls.

H. M. D.

Associated Liquids. W. A. KURBATOFF and G. G. ELISEEFF (*J. Russ. Phys. Chem. Soc.*, 1903, 41, 1422—1425. Compare Abstr., 1903, ii, 117, 120).—In order to throw light on the abnormal values of the Ramsay-Shields constant given by certain apparently normal liquids, the authors have examined acetic anhydride and ethyl malonate in this connexion.

* also *Zeitsch. physikal. Chem.*, 1910, 71, 385—400.

Acetic anhydride, for which Trouton's constant has the high value 23.9, is stated to give the normal value of the Ramsay-Shields constant, $K = d(\gamma M^{2/3})/dt = 2.129$, corresponding with a non-associated liquid. This value of K is confirmed by the authors' measurements, which give the mean result, $2.12 \pm 3\%$, in open and closed vessels.

A whole series of esters are known which are normal as regards their thermal data and their values of Trouton's constant, but give abnormally high values for the Ramsay-Shields constant. This is also found to be the case with ethyl malonate, which gives values of K varying from 2.20 to 2.56.

The results obtained indicate that the value of the Ramsay-Shields constant varies for different homologous series.

T. H. P.

Association of Glycerol. G. G. ELISEEFF and W. A. KURBATOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1426-1427).—The values of the Ramsay-Shields constant for glycerol at various temperatures are as follows: 0.63 at $35.2-64.8^\circ$; 1.10 at $64.8-74.3^\circ$; 1.50 at $74.3-101.4^\circ$, and 1.20 at $101.4-123.4^\circ$, the alteration with temperature being almost identical with that exhibited in the case of ethylene glycol. It hence appears that the degree of association of glycerol is not less than that of ethylene glycol. These results give no reason for expecting that the molecule of sugar is a simple one. But if the sucrose molecules are associated, as indeed all molecules containing hydroxyl groups appear to be, then the laws of osmotic pressure derived from a study of sucrose solutions should be modified, and there is exhibited also a possibility of an explanation of the coefficient i other than that given by Arrhenius.

T. H. P.

Adsorption of Ions. V. BOURNAT (*Compt. rend.*, 1909, 149, 1366-1368).—Dilute solutions of binary electrolytes, excluding acids, have a higher surface-tension than water; acids, however, lower the surface-tension. The action of acids is probably due to the accumulation of hydrions in the superficial layer, giving the same effect as in the capillary electrometer. In support of this explanation it is shown that the addition of a hundredth molecular weight of potassium ferrocyanide to a litre of $N/5$ -nitric acid increases the surface-tension to a considerable extent, whereas when added to a $N/5$ -solution of a binary salt the increase is only very slight. Perrin has shown that multi-valent ions diminish considerably the charge in a double layer, that is, that they accumulate in the surface layer, and in the experiment mentioned above they displace the hydrions and thus raise the surface-tension.

Comparing equimolecular solutions, the curve showing the relation between the molecular weights (abscissæ) of binary salts and the differences in the surface-tension (ordinates) of their solutions from that of water is a straight line. Monobasic acids also give a straight line lying below and parallel to that for the salts, the difference in the ordinates being 0.35 absolute unit for $N/10$ -solutions. Sodium and potassium hydroxide raise the surface-tension of water, but not to the same extent as binary salts; in this case, also, a straight line is

obtained, the difference in the ordinates being 0.25 unit. These differences are apparently proportional to the molecular concentrations of the solutions. Assuming that the diminution in the surface-tension is due to the accumulation of ions in the surface layer, it is shown that the number (n) of ions absorbed per unit surface is given by the formula $n = \mu c^2$, where c is the concentration, and μ is a constant depending on the ion. This formula is analogous to the general adsorption formula of Freundlich.

T. S. P.

Adsorptive Power of Hydroxides of Silicon, Aluminium, and Iron. III. Adsorption by Clay. II. PAUL ROHLAND (*Zeitsch. anorg. Chem.*, 1909, 65, 108—109; *Biochem. Zeitsch.*, 1909, 23, 278—280. Compare Abstr., 1909, ii, 27, 551).—A property of a Fraustadt clay, the analysis of which is given, is to adsorb unsaturated hydrocarbons when it has imbibed its maximum quantity of water. It is, however, impermeable to saturated hydrocarbon. By means of this clay, the unsaturated hydrocarbons can be separated from the saturated in American petroleum. The hydroxides of clays of this description (silicon, aluminium, iron, and titanium) can adsorb organic substances containing oxygen, such as alcohol and acetone, but prevent the diffusion of organic substances, such as carbon disulphide, toluene, etc., and hydrocarbons which do not contain oxygen, with the exception of the unsaturated hydrocarbons.

S. B. S.

Chemical Dynamics and the Colloidal State. I, II, and III. ALBERT REYCHLER (*J. Chim. Phys.*, 1909, 7, 362—368, 497—510. Compare Biltz, Abstr., 1904, ii, 324, 392).—The experiments made by Biltz on the removal of arsenious acid from its solution by shaking with colloidal ferric hydroxide led to the conclusion that the amount of acid removed (x) was related to the amount remaining in solution ($a - x$) by the equation $x^3 = K(a - x)$. The phenomena were attributed to adsorption, but were not further investigated mathematically.

The amounts of ferric oxide used by Biltz in all his experiments were sufficient to form a normal arsenite with 1.4 grams of arsenious oxide, whereas the amount of arsenious oxide actually adsorbed never exceeded 0.824 gram, even when almost four equivalents were available. If a normal arsenite is produced, its concentration would be represented by $x/1.4$, that of the free ferric hydroxide by $(1.4 - x)/1.4$, and of the free arsenious oxide, $(a - x)/3$. Assuming that normal ferric arsenite is hydrolysed in the usual manner for a salt of a weak acid and a weak base, the equilibrium will be $(x/1.4 - x)^4 = K_3(1.4 - x)/1.4^4 \cdot (a - x)/3$, where $K_3 = \frac{x^4/(a - x)}{(1.4 - x)}$.

If, on the other hand, only two of the basicities of arsenious acid are exercised, the constant is $K_2 = \frac{x^2/(a - x)}{(\frac{2}{3} \times 1.4 - x)}$.

It is shown that K_3 satisfactorily expresses Biltz's values up to the point where about one-half of the theoretically possible arsenious oxide is combined, and that above this K_2 gives a constant, pointing to the formation of some acid arsenite.

If the equivalent amount of arsenious oxide in Biltz's experiments is taken as 2.2 instead of 1.4, an even better constant (K_2) is obtained. It is not certain whether alumina has a similar affinity for arsenious oxide.

The author suggests that all so-called adsorption phenomena regulated by equations of the form $x^2/(a-x) = K$ may eventually be made amenable to the ordinary laws of chemical dynamics.

The experiments of Freundlich on the adsorption of various acids, etc., by blood-charcoal (Abstr., 1907, ii, 155, 939) can be considered as cases of chemical combination. Since, however, the basicity of charcoal is unknown, it is necessary to assume that 1 gram of charcoal is capable of combining with n -milli-equivalents of acid.

m -Grams of charcoal can therefore combine with mn -milli-molecules of a monobasic acid. If x milligram-molecules of acid be adsorbed, the degree of saturation of the charcoal is x/mn , and the unsaturated charcoal is $(mn-x)/mn$. If a is the initial concentration in the solution, $(a-x)$ is the final concentration. Assuming that the adsorption compound is hydrolysed like a salt of a weak acid with a weak base, $(x/mn)^2 = K_1(mn-x)/mn \times (a-x)$, whence $K_1 = (x/m)^2/(a-x)(n-x/m)$. By choosing a suitable value, for n , a very satisfactory constant, K_1 , can be obtained. The values are:

Acetic acid	$n=6$	$K_1=0.043$
Propionic acid	$n=5$	$K_1=0.139$
Dichloroacetic acid	$n=6$	$K_1=0.21$
Formic acid	$n=8$	$K_1=0.020$
Butyric acid	$n=6$	$K_1=0.30$
Chloroacetic acid	$n=4$	$K_1=0.33$
Benzoic acid	$n=4$	$K_1=21$
Sulphanilic acid	$n=5$	$K_1=0.21$

The strong acids, trichloroacetic acid and benzenesulphonic acid, do not give satisfactory constants; it is supposed that their adsorption compounds are not hydrolysed according to the same law. In the case of dibasic acids with only one active valency, $K_1 = (x/m)^2/(a-x)(2n-x/m)$, whereas if both valencies be active, $K_2 = \sqrt{(x/m)^3/(a-x) \div (n-x/m)}$.

With succinic acid both valencies are active: $n=10$ and $K_2=0.22$.

Citric acid acts as a tribasic acid: $K_3=0.16$ when $n=15$.

Bromine appears to follow the same adsorption law as monobasic acids, whereas methylamine follows a simple partition law. Adhesion, dissolution, etc., may in many cases superpose their effects on chemical adsorption.

The author's hypothesis is based on the theory that a large number of colloidal solutions may be considered as strongly basic or acidic salts.

For instance, the small proportion of hydrochloric acid which stabilises a solution of ferric hydroxide acts by combining with all the hydroxyls in turn, thus preventing the hydroxide from forming large complexes which on dehydration would be precipitated.

For every degree of dilution of the colloid sol there is a corresponding minimum of acid to prevent precipitation. All the known agents

for precipitating ferric hydroxide can be explained to act by disturbing the chemical equilibrium of acid, water, and ferric hydroxide.

Colloidal silica can be considered as a very acidic sodium silicate, and its properties can all be explained on chemical grounds.

The phenomena of cataphoresis and anaphoresis, the precipitation of colloids by electrolysis, may be due to the transfer of water to anode or cathode respectively, the colloid appearing to travel in the reverse direction.

R. J. C.

Adsorption of Arsenious Acid by Ferric Hydroxide. WILHELM BILTZ (*J. Chim. Phys.*, 1909, 7, 570—574).—It is shown that Reychler's explanation (preceding abstract) of the author's observations relating to the absorption of arsenious acid by ferric hydroxide is untenable. This explanation is based on the assumption of the formation and hydrolytic decomposition of ferric arsenite.

New experiments have been made in which varying quantities of the hydroxide were shaken up with the same volume of a solution of arsenious acid of determined concentration. If z denotes the quantity of arsenious oxide taken up by m grams of the hydrogel, and x is the quantity which remains in solution, the observed results can be satisfactorily represented by the equation :

$$\log z/m = 0.237 \log x + \log k.$$

From this the author concludes that the removal of arsenious acid from the solution by the ferric hydroxide is a pure adsorption phenomenon.

H. M. D.

Thermodynamics of the Capillary Layer. GERRIT BARKER (*Zeitsch. physikal. Chem.*, 1909, 68, 684—692).—A mathematical paper. The author indicates certain errors very often committed in applying thermodynamical considerations to the capillary layer.

When the capillary layer is considered by itself, instead of the usual equation: $dQ = d\epsilon - Hds$ (where dQ is the heat absorbed in varying the surface, $d\epsilon$ is an energy difference, H is the surface-tension, and ds the change of surface), the equation $dQ = d\epsilon + p_x dv - Hds$ must be used, where p_x is the vapour pressure, and v the specific volume of the capillary layer. The last equation is the correct expression for the specific heat of the capillary layer per unit of mass. Nothing is known as to the variation of this specific heat with temperature.

The energy equation obtained when a vessel filled with liquid, vapour, and the capillary layer as transition layer is considered, differs from that deduced for a thin sheet.

G. S.

Relationship between Physical Properties of Solutions. I. Density and Electrical Conductivity of Aqueous Solutions of Salts. ADOLF HEYDWEILLER (*Ann. Physik*, 1909, [iv], 30, 873—904).—From an examination of the data for a large number of aqueous solutions of electrolytes, it is shown that a connexion exists between the density of a solution and that of the solvent, which can be expressed by the equation $\Delta = B + (A - B)x$. In this equation, Δ denotes the percentage change in density per gram-equivalent of the dissolved

electrolyte, i is the ratio of the equivalent conductivity of the given solution to the conductivity at infinite dilution, and A and B are constants. A and B represent respectively the percentage changes in density which are caused by one gram-equivalent of ionised and non-ionised electrolyte; $A - B$ represents the influence of ionisation on the density of the solution. The values of A and B are tabulated for a number of electrolytes.

For certain electrolytes, the values of B indicate that the volume of the undissociated electrolyte in solution is the same as that of the salt in the solid state. In other cases, changes in volume take place on solution. The contractions which are found in the case of salts which form hydrates in the solid state indicate that hydrated molecules are also present in the aqueous solutions.

Ionisation of the electrolyte is always accompanied by an increase in density, and this is found to become greater as the sum of the mobilities of the constituent ions increases. The observed contraction is shown to be probably due to a diminution in the volume of the water.

The values of A exhibit additive relationships, and ionic moduli are calculated, by means of which it is possible to calculate the influence of the ionised portion of any electrolyte on the density of its aqueous solution.

Certain electrolytes are abnormal, in that they do not agree with the relationship $\Delta = B + (A - B)i$. The anomalous behaviour is traced in some cases to the formation of complex ions in the more concentrated solutions, and to the large affinity of the dissolved salts for water.

H. M. D.

Condition of Equilibrium between a Dilute Solution and the Pure Solvent Separated by a Semi-permeable Diaphragm or by the Vapour of the Solvent. GIOVANNI GUGLIELMO (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 536—544).—Making use of two relations which were obtained by van der Waals (see *Die Continuität des flüssigen und gasförmigen Zustandes*), and which express the condition of equilibrium of a large number of molecules (considered as material points) in perpetual motion and attracting one another, the author derives (1) in two forms, the condition of equilibrium of the molecules of a chemically homogeneous liquid, and (2) the equilibrium conditions for a chemically heterogeneous liquid—solvent and solute; (3) the condition of equilibrium between pure solvent and solution separated by a semi-permeable surface. With the aid of the results thus obtained, the following questions are discussed: independence of the molecular attraction on the mass of the molecules, and a hypothesis on the nature of this attraction; causes of the lower vapour pressure of solutions compared with the solvents, and of the equality of vapour pressure for equimolecular solutions; influence of the curvature of the surface of a liquid on its vapour pressure.

T. H. P.

Binary Mixtures and Concentrated Solutions. Remarks on Dolezalek's Paper. THOMAS S. PATTERSON (*Zeitsch. physikal. Chem.*, 1909, 67, 572—574. Compare Dolezalek, *Abstr.*, 1909, ii, 22).—It is

shown that the theoretical densities of mixtures of chloroform and acetone calculated by Dolezalek are incorrect, as they were obtained by dividing the respective densities of the components by the molecular fraction of the component in the mixture instead of by the usual method. The observed density of a particular mixture of chloroform and acetone only differs very slightly from the theoretical value; the deviation is only one-ninth of that given by Dolezalek, and the conclusions of the latter investigator therefore require revision.

G. S.

Existence and Properties of Disperse Systems in the Region Separating Colloidal and Crystalloidal Solutions. TOR SVEDBERG (*Zeitsch. Chem. Ind. Kolloide*, 1909, 6, 318—325. Compare Abstr., 1909, ii, 389).—Experiments are described which show that the absorption of light by a gold hydrosol increases as the size of the colloidal particles increases. By raising the temperature of a ruby-red hydrosol or by the addition of electrolytes, the particles were caused to coagulate, and measurements of the colour intensity showed a gradual increase in the absorptive capacity of the hydrosol. The addition of a non-electrolyte was found to be without influence on the absorption.

By the reduction of a solution of gold chloride by means of hydrazine in presence of gelatin (free from electrolytes) as protective colloid, gold hydrosols consisting of extremely small particles can be obtained. The intensity of the colour of the hydrosol obtained in this way is much smaller than that of the hydrosol obtained under similar conditions in the absence of the protective colloid. The action of this consists in reducing the rate of coagulation of the hydrosol, and it is shown that the activity of the gelatin is approximately proportional to its concentration.

Gold hydrosols prepared in different ways exhibit considerable differences in respect of the position and the intensity of the absorption maximum. This is found to depend on the size of the colloidal particles. As the size diminishes, the absorption maximum shifts towards the region of smaller wave-lengths. For the most highly disperse hydrosols this maximum is in the ultra-violet, and approximates to the position of the maximum for a solution of gold chloride.

H. M. D.

Theory of Colloids. JACQUES DUCLAUX (*J. Chim. phys.*, 1909, [vii], 405—446. Compare Duclaux, Abstr., 1909, ii, 303; Maltana, *ibid.*, 473; Pappada, *ibid.*, 473).—The author develops the theoretical ideas already put forward by him into a complete theory of colloids. The physical theory, which postulates that the stabilising ions in a colloidal solution are permanently combined with the colloid particles, and that the whole osmotic pressure is due to colloid particles acting as molecular units, fails to explain the difference in properties when one stabilising ion is substituted for another. According to the chemical theory put forward by the author, colloid particles are very large multivalent ions forming salts with the stabilising ions which surround them, but which are capable of super-adding their osmotic

pressures, conductivities, etc., to that of the nucleus granules or micella (compare Reichler, this vol., ii, 105). The degree of ionisation will vary with the nature of the stabilising ion. For example, ferric hydroxide stabilised with sulphuric acid has a much higher osmotic pressure than the same colloid stabilised with hydrochloric acid.

It is shown that if the colloidal micella is assumed to be exactly comparable to an ionisable salt, the osmotic pressures calculated from the conductivities and ionic mobilities of the solutions are about double the experimental osmotic pressures. The measurements were all made on solutions with a very pure intergranular liquid (compare, however, Malkitano, *loc. cit.*), and a small correction was subtracted for the conductivity of the intergranular liquid. The ionic mobilities of the colloid granules were determined by passing a direct current through the solution and afterwards analysing the liquids in the anode and cathode chambers, it being assumed that no transference of water had occurred. The ultramicroscope is not available here, because colloids with an appreciable osmotic pressure are so small as to be almost invisible.

When a colloidal solution is dilute, the micella are so widely separated that the ions surrounding each one are never attracted from it, but the whole comprises a stable, almost neutral sphere. On establishing an electric field, the ions all crowd to one side of the sphere and the parent granule to the other. Since the voltages required for electrolysis are small, it follows that only a few of the ions become detached. When the solution is concentrated, the micella approach each other, and ultimately their neutral spheres intersect. Each micella will then facilitate the ionisation of its neighbours, a kind of Grotthuss's chain being set up. It follows that as a colloidal solution is concentrated, its "molecular" conductivity increases. This is shown to be the case with ferric hydroxide and gum arabic. The degree of ionisation of a colloid does not mean the proportion of granules ionised, but the average extent to which each granule is ionised. Knowing the number of stabilising ions, the degree of micella ionisation can be calculated. It varies in the author's experiments from 0.008 in copper ferrocyanide to 0.88 in gum arabic. If the intergranular liquid contains electrolyte, this must have an ion in common with the micella, and will influence its ionisation.

When the degree of ionisation of the micella, the ionic velocity, and the viscosity are known, the radius of the micella can be calculated with the aid of Stokes' theorem. This varies from 0.55μ in tungstic acid to 5.2μ in Prussian-blue, the number of free ions per micella being 2.9 and 24 respectively.

These values are in accord with the relative retention of the colloids by collodion, and are also of the same order as the radius, $< 1\mu$, found by Zsigmondy for colloidal gold particles.

The molecular weights of the colloids, calculated from their micella radii are: tungstic acid 1900, thorium hydroxide 7000, gum arabic 16,000, ferric hydroxide 115,000, copper ferrocyanide 700,000, Prussian-blue 1,000,000.

The neutral sphere probably has a radius about ten times that of

the micella, that is to say, on an average an ion does not move further than $10\mu\mu$ from the micella.

Direct measurements have been made of the osmotic pressures of ferric hydroxide, copper ferrocyanide, Prussian-blue, thorium hydroxide, gum arabic, and caramel with collodion membranes. The results confirm those obtained by the filtration method (Abstr., 1909, ii, 303), and clearly show that the osmotic pressure of a colloid increases more rapidly than the concentration. In very dilute solution each micella with its ions complete acts osmotically as one molecular unit.

As the concentration increases, it may attain by splitting off of ions an osmotic value of 8 or more.

R. J. C.

General Equation of State. KARL DRUCKER (*Zeitsch. physikal. Chem.*, 1909, 68, 616—636).—A theoretical paper. A general equation of state is deduced on the assumption that the gas laws hold for gases and pure liquids in general, and that the deviations are to be accounted for on purely chemical grounds, that is, on the formation of complex molecules (polymerides). On this basis the general gas equation $pv = RT \cdot \Sigma n$ leads to the equation: $p/RT = \Sigma n/v = \Sigma c = c_1 + c_2 + c_3 + \dots$ (1), where $\Sigma c = c_1 + k_2 c_1^2 + k_3 c_1^3 + \dots$. In this equation c_1, c_2 , etc., represent the respective partial concentrations of the simple and complex molecules; k_1, k_2 , etc., represent the respective equilibrium constants, and the other symbols have the usual significance. It is assumed in deducing this equation that equilibrium between simple molecules and their polymerides is established instantaneously.

In equation (1) the coefficients are necessarily positive, and it appears at first sight as if it applies only to cases where the compressibility is too great. Although this difficulty can theoretically be got over, it has been considered advisable to insert a volume correction (analogous to that of van der Waals) in equation (1). The equation is then tested by application to the data for ethyl ether, methyl alcohol, and other vapours given by Ramsay and Young and others, and simplified forms of it are found to give satisfactory results.

The application of these considerations to liquids leads to the conclusion that a liquid under ordinary conditions consists of a dilute solution of unimolecules in complex molecules. The fact that this result is in apparent conflict with the method of determining the molecular complexity of liquids due to Eötvös-Ramsay-Shields, based on surface-tension measurements, is not regarded as an insuperable objection, as the method in question has no purely thermodynamic basis. The author considers that liquids, such as water, usually regarded as complex, are really comparatively simple.

Provisional suggestions are made for determining the partial concentrations in liquids.

G. S.

Demonstration of the Phase Rule. R. BOULOUCH (*Compt. rend.*, 1909, 149, 1377. Compare Abstr., 1909, ii, 802).—The author maintains his criticisms of Müller's demonstration of the phase rule,

pointing out that Müller has confused three things which are essentially distinct, namely: (1) the actual changes taking place in a system not in equilibrium; (2) the virtual changes which one imagines to take place in a system in equilibrium; (3) the atomic interchanges occurring, according to the atomic theory, in a system in equilibrium.

T. S. P.

Invariant Systems and the Regularity of Composition of Certain Eutectics. ALEX. GORBOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1241—1300).—The author discusses the phase rule and the composition of eutectic mixtures, a large number of examples from the work of various investigators being considered. The principal results arrived at are as follows.

One of the fundamental propositions of chemical mechanics is that the laws by which material systems are characterised are determined, not by the number of their components, but by the number of effective degrees of freedom.

Examination of the compositions of eutectics formed by the elements and by chemical, "molecular," and "complex" compounds shows that the composition of any eutectic corresponds with a chemical compound formed by the elements occurring in the eutectic, which may hence be expressed by a chemical formula with rational indices. So that eutectics obey not only the law of constant composition, but also the law of multiple proportions.

Not only may the composition of a eutectic formed by two independent components capable of giving chemical compounds melting without decomposing be expressed by a chemical formula, but this formula is often constructed according to a simple rule—equal masses of one of the two components being distributed in both solid phases of the eutectic. Thus, if the two components, A and B , form the compounds $A + xB$ and $A + yB$, melting without decomposing, then the eutectic between A and $A + xB$ is expressed by the formula $2A + xB$, and that between $A + xB$ and $A + yB$ by the formula $(yA + xyB) + (xA + xyB)$ or $(x + y)A + 2xyB$, and so on. Excluding the limiting eutectics answering to the general formula, $2A + xB$, in all the others, expressed, for example, by $(x + y)A + 2xyB$, in both solid phases that independent component is distributed in equal masses which possesses the more basic chemical character. The latter in the eutectics formed by crystallo-hydrates of sulphur dioxide, hydrogen chloride, hydrogen iodide, nitrogen pentoxide, copper nitrate, magnesium chloride, ferrous nitrate, and ferric chloride is water, and in the metallic eutectics the more alkaline metal.

In every case where a chemical compound of two components does not melt without decomposing, but exhibits a transition point below the melting point, its solubility in one of the components is lower, sometimes very considerably lower, than is required by the above rule; in such cases, this component consequently occurs in excess in the eutectic.

For the large numbers of experimental data from which these conclusions are drawn and for references given, the original must be consulted.

T. H. P.

Influence of Centrifugal Force on the Equilibrium of Chemical Systems. A. V. DUMANSKY (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1306—1308).—When a concentrated solution of cadmium iodide is subjected to centrifugalisation in a tube closed with a cork, a brown precipitate containing cadmium and iodine is deposited, whilst aqueous hydrogen iodide under similar conditions gives a deposit of iodine. The author's results seem to indicate that the cork acts as a catalyst.

Also, centrifugalisation of solutions of ferric chloride and mercurous nitrate produces a marked increase in the electrical conductivity of the solutions, the increased values persisting after removal of the centrifugating force and mixing of the liquids. Since all the compounds used in his experiments are readily decomposed by water, the author suggests that such decomposition may occur to a slight extent, and that one of the products of the decomposition, being the heavier, may be readily removed from the sphere of action by the centrifugalisation. Thus, with ferric chloride, the ferric hydroxide formed by the hydrolytic dissociation would pass to the periphery of the centrifuge, and thus permit of the hydrolysis of further quantities of ferric chloride; the hydrochloric acid formed by the hydrolysis would cause the increased conductivity observed.

Colloidal solutions of antimony sulphide and ferric hydroxide deposit precipitates when subjected to centrifugalisation. T. H. P.

Chemical Affinity. III. Solution-affinity of Binary Systems. II. Sulphuric Acid and Water. J. N. BRÖNSTED (*Zetsch. physikal. Chem.*, 1909, 68, 693—725).—The theoretical conclusions discussed in the previous paper (compare Abstr., 1909, ii, 29) are now tested by application to the system sulphuric acid-water.

The heat of admixture of sulphuric acid and water has been determined over the whole range of concentrations, and as large amounts of the substances were used, the results are probably very accurate; they are represented in tabular form in various ways. The heat of formation of 1 mol. of monohydrate is 6710 cal. The m.p. of pure sulphuric acid on the hydrogen scale is 10.49°. The results obtained are in good agreement with those of Pfundler and of Pickering (*Trans.*, 1890, 57, 94), but not with those of Thomsen (*Thermochemische Untersuchungen*); it is probable that Thomsen's "pure" acid contained a little water. From the results, the differential curves for the heats of admixture are determined by means of the equations given in the earlier paper.

The solution-affinity of the components throughout the whole range of concentrations is then determined from the combined results of *E.M.F.* measurements, of vapour-tension measurements, and of freezing-point determinations. The reaction, the *E.M.F.* of which has been determined, is the formation of sulphuric acid by the reduction of mercurous sulphate by hydrogen, the cell being built up as follows: $H_2 \mid H_2SO_4 \mid Hg_2SO_4 \mid Hg$. Measurements have been made between 15° and 80° with varying proportions of acid, and the affinity is calculated from the results by means of the Helmholtz equation in the usual way.

As regards vapour-pressure measurements, the results of Tammann (*Zeitsch. physikal. Chem.*, 1888, 2, 42) at 100°, and of Dieterici (*Ann. Phys. Chem.*, 1893, [ii], 50, 47) at 0°, have been supplemented by measurements at 20° and 30° with a special form of apparatus.

In connexion with the calculation of solution-affinity from freezing-point determinations with the help of thermal constants, it has been found that the heat of fusion of sulphuric acid is $2485 + 6.1t$ calories per mol., and that of the monohydrate, $4290 + 18.8t$ calories. From these results the differential solution-affinity curves for water and acid respectively have been obtained, and for comparison are plotted on the same diagram with the corresponding curves for the heat of admixture. The forms of the curves are very different from the ideal type, due to chemical reaction between water and acid.

As regards the sulphuric acid curve, A , the solution-affinity is greater than U , the heat of admixture, for $x=1$ (x is the molar proportion of acid in the mixture); the curves intersect at $x=0.53$, where $A=U=1400$ cal., beyond which the A curve is lower than the U -curve, until they again intersect at $x=0.006$, when $A=U=17,000$ cal. For water the affinity and heat of reaction curves practically coincide for concentrations between 0.1 and 0.3.

The values found are throughout in accord with the general thermodynamic equation: $A - U = T \times dA/dT$ (where the symbols have the usual significance). G. S.

Affinity of Sodium Phosphate for Water. PAUL TH. MÜLLER (*J. Chim. Phys.*, 1909, 7, 534-539).—The theorem recently published by Nerst (Abstr., 1907, ii, 153) correlating affinity with temperature in condensed systems is applied to the affinity of sodium phosphate for water.

The affinity of the hydrate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, for its water is given by the formula $A = 1.985T \log f/f'$ cal., where f and f' are the vapour pressures of pure water and hydrate respectively at temperature T . Nerst's equation gives $A = Q_0 - \alpha T^2 - \beta T^3/2$, where Q_0 is the heat of hydration at absolute zero. The values of A in the first formula are calculated from Frowein's measurements of the vapour pressure of the hydrate between 6.8° and 27.00°. If $Q_0 = 1200.53$ cal., $\alpha = 0.0119827$, and $\beta = 0$, Nerst's formula gives values agreeing with Frowein's within 0.35%. The heat of hydration at any temperature is equal to $Q_0 + \alpha T^2 + \beta T^3$. Hence the heat of hydration of sodium phosphate at 18° should be 2215.3 cal., whereas Thomson and Pfaundler obtained the values 2234 cal. and 2241 cal. by direct measurements. When the affinity for water (A) is zero, $(Q - \alpha T^2) = 0$, whence $T = 316.5^\circ$ abs. It follows that at 43.5° the phosphate becomes anhydrous. Extrapolation of Frowein's results indicates that at about this temperature the vapour pressure of the phosphate begins to exceed that of water. R. J. C.

Chemical Kinetics. OTTO SACKUR (*Zeitsch. Elektrochem.*, 1909, 15, 865. Compare Trautz, Abstr., 1909, ii, 651).—Trautz's equations for the velocity of a reaction are obtained, essentially, by dividing the well known equation $d \log K/dT = Q_0/RT^2$ into the two equations: $d \log k_1/dT = q_1/RT^2$ and $d \log k_2/dT = q_2/RT^2$, where k_1 and k_2 are the

velocity constants of the two opposite reactions, and q_1 and q_2 are the sums of the heats of formation of the molecules taking part in them. The equations are then integrated by means of Nernst's theorem. The author points out that these partial equations are not necessarily correct, because a pair of equations of the form $d \log k/dT = q_1/kT^2 + \phi(T)$, where $\phi(T)$ is any function of the temperature, would equally, when subtracted from each other, give the original equation. The assumption that $\phi(T) = 0$, although possible, is not necessarily true. T. E.

Temperature-coefficient of Chemical Reaction Velocities.
IV. Addendum. MAX TRAUTZ (*Zeitsch. physikal. Chem.*, 1909, 68, 637—638. Compare Abstr., 1908, ii, 924; 1909, ii, 557; this vol., ii, 24).—Sackur's adverse criticisms (compare preceding abstract) of the author's work, in so far as they are new, are not valid. G. S.

Residual Affinity and Additivity. Part II. WALTER PETERS (*Ber.*, 1909, 42, 4826—4836).—The observations on the union of ammonia with various salts (compare Abstr., 1908, ii, 937) have been further extended. In the platinum complex salts, the additive power (for ammonia) cannot be considered as an additive property of the component salts. A consideration of the additive ammonia compounds of copper and cadmium platinichlorides shows that the complex salt either adds on ammonia as a whole, or else the anion and cation each exert their own particular residual affinity. The compounds of copper and cadmium behave very similarly to each other, as also do the compounds of bivalent manganese and zinc.

Metals belonging to the same periodic group show the same or very similar behaviour. Uranium tetrachloride has a greater additive power for ammonia than has uranyl chloride. Replacement of one halogen by another has no influence on the residual affinity.

Werner's co-ordination number six, or a multiple thereof, holds for half of the salts mentioned in this and the previous communication.

Many salts which are hygroscopic no longer show this behaviour after the addition of ammonia; the fact that a salt is hygroscopic therefore depends on the exertion of subsidiary valencies.

The following table gives a summary of the results at the ordinary temperature: I giving the number of mols. of ammonia absorbed, and II the number retained after evacuation.

	I.	II.		I.	II.
Calcium platinichloride	12	6	Ammonium palladiochloride	5	4
Barium platinichloride	6	5	Palladium iodide	0 (at 0°)	2
Zinc platinichloride	11	7	Rhodium chloride	4	3
Manganese platinichloride	11	7	Ruthenium chloride	3	3
Copper platinichloride	18	6	Ruthenium bromide	3	2
Cadmium platinichloride	18	6	Cuprous chloride	2	1
Cobalt platinichloride	12	10	Cuprous iodide	3	0
Nickel platinichloride	12	10	Silver nitrate	3	2
Sodium platinichloride	4	3	Chromous chloride	6	3
Sodium platinibromide	6	5	Uranium tetrachloride	3	3
Platious iodide	5	4	Uranyl chloride	2	1
Platinic chloride	6	5	Manganous chloride	6	2
Platinic bromide	6	5	Manganous iodide	6	5
Palladium chloride	5	4	Manganous sulphate	6	2
Sodium palladiochloride	5	4			

Neither hydrogen chloride nor phosphine combines with any dry inorganic salt. Acetylene is absorbed only by cuprous chloride. Ethylene gives no additive products; its absorption by ferrous and platinous chloride in ethereal or hydrochloric acid solution only takes place when these chlorides are formed by reduction of the corresponding ferric and platinic chlorides. Carbon monoxide was not absorbed by any of the salts investigated under the particular conditions of experiment.

T. S. P.

Eder's Solution. I. CHR. WINTHER (*Zeitsch. wiss. Photochem.*, 1909, 7, 409—441).—The rate of the photochemical reaction between mercuric chloride and ammonium oxalate in aqueous solution is increased by ceric salts and potassium ferrioxanide, and decreased by cupric salts, potassium tin chloride, and many organic colouring matters. Potassium iodide in small quantity accelerates the reaction, but when this is present in excess, the velocity of the reaction diminishes.

In order to obtain information relative to the nature of the catalytic effect, the author has examined the behaviour of chlorine, potassium permanganate, and more especially ferric salts. In the case of chlorine the catalytic phenomenon is traced to the inducing effect of the reaction between chlorine and ammonium oxalate on that between the mercuric salt and the oxalate. The action of potassium permanganate is found to be accompanied by a period of induction, during which the permanganate is reduced to a manganic salt, which then accelerates the photochemical change. The mode of action of this is in all probability similar to that of ferric salts.

The numerous experiments made on solutions containing iron salts show that the catalytic effect is very largely dependent on the amount of oxygen which is present. In the absence of oxygen, the catalytic process can be resolved into two stages, in one of which the rapid photochemical reduction of ferric oxalate is involved, whereas the other consists in the inducing effect of the oxidation of the ferrous oxalate formed in the photochemical reduction process. In presence of oxygen, the process is complicated by reason of the action of the oxygen on the reduced ferric salt.

In support of this view it is found that the rate at which mercurous chloride is precipitated from a solution containing a given amount of ferrous salt increases as the amount of oxygen in the solution diminishes. For a given quantity of ferrous salt, the total amount of mercurous chloride precipitated increases as the oxygen concentration diminishes. Ferric salts diminish the rate of the reaction. For a given ratio between ferric and ferrous salts, the retarding effect increases rapidly with the total amount of iron in the solution. These observations are in accord with the fact that maximum photo-sensitiveness is obtained for a particular iron concentration. Since the retarding action of ferric salts increases when the amount of oxygen in the solution diminishes, the iron concentration corresponding with maximum sensitiveness diminishes with the oxygen concentration.

The rate of precipitation of mercurous chloride from Eder's solution

is recommended as a means of estimating small quantities of dissolved oxygen.

H. M. D.

Vacuum Correction of Weighings Applied to Atomic Weight Determinations. PHILIPPE A. GUYE and N. ZACHARIADIS (*Compt. rend.*, 1909, 149, 1122—1123. Compare Abstr., 1909, ii, 989).—The authors have determined previously the magnitude of the error made in reducing weighings to vacuum values, through the presence of condensed air on the surface of the substance. These calculations have now been revised after taking into account another source of error. The new numbers, together with the results of fresh determinations for other common substances, are given in tabular form. The results were obtained by weighing a flask in air (*a*) exhausted of air, (*b*) full of air, (*c*) containing air and the substance, (*d*) containing the substance only.

The apparent weight of the salt in air is reduced to the vacuum value by the usual method, and compared with the "actual weight in vacuum" given by $(d - a) - p$, where p is the loss of weight in the air of the standard weights. A further correction should be made for the air condensed on the surface of the standard weights.

The "actual weight in vacuum" was in each case found to be higher than the calculated value, the difference ranging from 1 mg. in the case of silver bromide to 25 mg. in the case of sodium chloride per 100 grams. In the case of silver, however, the numbers were the same.

W. O. W.

The Fundamental Constant of Atomic Vibration and the Nature of Dielectric Capacity. WILLIAM SUTHERLAND (*Phil. Mag.*, 1910, [vi], 19, 1—25).—On the assumption that positive and negative electrons are associated in pairs, and are revolving round one another in such a way that each pair has an average electric moment, it follows that if these moments are similarly directed, the atom as a whole will have an electric moment, and can be investigated as a uniformly electrified sphere. It is shown that the internal electric fields cause atomic vibrations, and that the atomic vibrator can be regarded as the single electron which is involved in the explanation of the Zeeman effect. The common constant which appears in Rydberg's formulae for the series lines of many elements is discussed in terms of this conception of the atomic vibrator. An explanation of dielectric capacity in terms of the electron theory is given, and it is shown that Balmer's formula relating to spectral structure can be interpreted on a kinematical basis.

H. M. D.

Molecular Diameters. WILLIAM SUTHERLAND (*Phil. Mag.*, 1910, [vi], 19, 25—26).—On the basis of the value 2.77×10^{19} obtained by Rutherford for the number of molecules in 1 c.c. of a gas under standard conditions, the author has recalculated a series of molecular diameters with the following result: H₂ 2.17, He 1.02, CO 2.74, C₂H₄ 3.31, N₂ 2.95, NO 2.59, O₂ 2.71, A 2.66, CO₂ 2.90, N₂O 3.53, Cl₂ 3.76×10^{-8} cm.

H. M. D.

Liquid Extraction with the Aid of Soxhlet's Apparatus. PADASU SAIKI (*J. Biol. Chem.*, 1909, 7, 21—22).—A modification of Soxhlet's apparatus, is described and figured for the extraction of liquid material with ether. W. D. H.

Apparatus for Evaporating Ethereal Solutions. GILBERT P. HARDWOOD (*Analyst*, 1909, 35, 16).—The one end of an inverted siphon has the shape of a funnel, and the other end projects several inches below the level of the ethereal solution to be evaporated. The watch-glass containing this is placed under the funnel-shaped opening, and by applying suction to the long arm, the ether vapour siphons over, and the residue is finally deposited in a small space in the centre of the watch-glass.

The same means may be adopted for concentrating an ethereal solution in a test-tube or beaker by gradually lowering the funnel of the siphon as the ether evaporates. L. DE K.

Inorganic Chemistry.

Condition of Dissolved Iodine. PERCY WAENTIG (*Zeitsch. physikal. Chem.*, 1909, 68, 513—571. Compare Beckmann, *Abstr.*, 1907, ii, 340).—The investigation of solutions of iodine in a large number of solvents has led to the conclusion that in all the solutions iodine is partly combined with the solvent according to the reversible equation: $\text{SoI}_2 \rightleftharpoons \text{So} + \text{I}_2$ (So = solvent); for the violet solutions, the spectra of which approximate to that of iodine vapour, the amount of combination is much less than for the brown solutions.

These conclusions are mainly based on spectroscopic observations, and, in particular, the effect of change of temperature on the spectra has been fully investigated. On heating the violet solutions, the absorption band becomes displaced towards the red end of the spectrum, in other words, towards that of iodine vapour, and is displaced in the opposite direction on cooling. The spectra of many of the brown solutions tend to become permanently altered on heating, a result which speaks in favour of considerable association between iodine and solvent. The view that there is only a difference in degree between violet and brown solutions is further supported by the fact that brown solutions in thiophen and in sulphur dioxide become violet on heating, and regain the original colour on cooling.

The conclusion to be drawn from the displacement of the equilibrium with temperature that the heat of formation of the compound must be positive, is supported by observations on the effect of temperature on the solubility of iodine, and on its heat of solution in different solvents. Although the heat of solution is negative in all the solvents examined except pyridine, the heat absorption is much less for brown than for violet solutions. Moreover, cryoscopic investigations with iodine and a "solvent" dissolved together in an indifferent solvent show that the

depression is so much the smaller the greater the degree of combination according to the above considerations (compare Hildebrand and Glascock, *Abstr.*, 1909, ii, 225). A compound with pyridine, of the formula PyI_2 , has been isolated.

The influence of dilution on the absorption spectra has been measured for two kinds of light, and it was found that, contrary to the requirements of the law of mass-action, the ratio of the absorption for both kinds of light increases with dilution. This is probably connected with ionisation of the additive compound, as many of the solutions have a considerable molecular conductivity, which increases with the dilution.

The observations on the nature of the absorption bands, and of their displacement with temperature, are satisfactorily accounted for on the assumption that there is a maximum of absorption for the additive compound in the ultraviolet, and that the absorption due to the compound is more or less affected by the absorption band due to free iodine.

The partial vapour pressures of the components in boiling solutions of iodine in ether, carbon disulphide, chloroform, carbon tetrachloride, and benzene have also been determined, and the results, considered from the point of view due to Dolezalek (*Abstr.*, 1909, ii, 22), support the above conclusions. Even at the boiling point there is considerable association between iodine and solvent in the brown solutions.

The molecular freezing-point depression for carbon tetrachloride is 299. G. S.

Production of Ozone by Ultraviolet Light. EDMOND VAN AUBEL (*Compt. rend.*, 1910, 150, 96—98).—The following correction should be made in the previous paper (this vol., ii, 28). In the experiments where water was used to absorb the ozone produced, the resulting solution contains hydrogen peroxide, the presence of which was detected by its action on a photographic plate. The presence of hydrogen peroxide in the water proves the formation of ozone in the air by the action of the ultraviolet light. T. S. P.

Dissociation Isotherms of Sulphur between 300° and 850°. GERHARD PREUNER and W. SCHUPP (*Zeitsch. physikal. Chem.*, 1909, 66, 129—156).—By means of the quartz-glass manometer described by Aegg and Johnston (*Abstr.*, 1908, ii, 157), the authors have determined the density of sulphur vapour at nine temperatures between 300° and 850° and within wide limits of pressure. The results cannot be reconciled with the assumption that only S_8 and S_2 molecules are present, but indicate that above 30 mm. pressure only S_8 , S_6 , and S_4 molecules are present. At pressures lower than 30 mm. it is possible that S_1 molecules are also contained in the vapour.

From the displacement of the different equilibria with temperature, it is calculated that in the reaction $3\text{S}_8 = 4\text{S}_6$, 29,000 calories are absorbed, and in the other reaction, $\text{S}_8 = 3\text{S}_2$, 64,000 calories are absorbed. Similarly, the change of gaseous S_8 to 4S_2 absorbs 95,000 calories. From the most trustworthy results on the variation of the vapour pressure of sulphur with the temperature, it is calculated that the heat

of vaporisation, $8S[\text{solid}] \rightarrow S_8(\text{gaseous})$, is 20,000 calories, hence for the reaction $8S[\text{solid}] \rightarrow 4S_2(\text{gaseous})$, 115,000 calories are absorbed. Otherwise expressed, it requires about $115,000/4 = 28,800$ calories to transform 64 grams of solid sulphur into gaseous S_2 .

On the assumption that S_8 is identical with S_4 , the modification of sulphur insoluble in carbon disulphide, the proportion of S_4 in saturated sulphur vapour is calculated from the density results at different temperatures, and compared with the values determined directly by Gal (Abstr., 1893, ii, 455) and by Kruyt (Abstr., 1908, ii, 1028). The authors' results are in excellent agreement with those of Gal, but not with those of Kruyt.

G. S.

Action of Hydrogen on Sulphur or Selenium in Presence of Another Element. HENRI PÉLABON (*J. Chim. Phys.*, 1909, 7, 447—463).—Excess of pure sulphur or of sulphur containing less than 2/3 atomic proportion of arsenic when heated at 610° in hydrogen gives a gaseous mixture containing about 98% of hydrogen sulphide. When the proportion of arsenic is increased until the sulphur is saturated at approximately the composition $SA_{2.5}$, the amount of hydrogen sulphide decreases regularly to 78%. Further addition of arsenic, which remains as a separate phase, does not decrease the amount of hydrogen sulphide produced. The uniphase solutions of arsenic in sulphur give a greater proportion of hydrogen sulphide the less the pressure of hydrogen, but mixtures containing a free arsenic phase always give 78% of hydrogen sulphide.

The results obtained with mixtures of arsenic and selenium are analogous, but the proportions of hydrogen selenide are in all cases much lower.

Addition of selenium or tellurium to mixtures of sulphur and arsenic promotes the formation of hydrogen sulphide, but to a less extent than an equivalent amount of sulphur itself.

Selenium produces a similar effect on mixtures of sulphur and antimony, but tellurium is here without influence.

The addition of antimony to sulphur makes no change at first in the amount of hydrogen sulphide (98%), but when 43—90 atoms of antimony are present per 100 of sulphur, the liquid consists of two phases, antimony sulphide saturated with antimony, and antimony saturated with its sulphide. Whilst these two phases are present, the proportion of hydrogen sulphide produced is about 60%. With larger proportions of antimony, the hydrogen sulphide rapidly decreases towards zero.

The phenomena with mixtures of selenium with antimony, bismuth, tin, and thallium are similar to those obtained with selenium and arsenic. Silver and copper, on the other hand, which form stable selenides solid at the temperature employed, entirely prevent the formation of hydrogen selenide when their proportions exceed Ag_2Se and Cu_2Se .

R. J. C.

Preparation of Colloidal Solutions of Selenium. ALFREDO ROCCETTINO (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 544—551).—In preparing colloidal solutions of selenium by the method of Müller

and Nowakowski (Abstr., 1906, ii, 18), the author finds that, at the same time as a red coloration forms in the liquid near the cathode, the current intensity exhibits a continuous increase which begins immediately the circuit is closed. If the liquid in the cell is shaken, the current intensity falls sharply, but rises to the original value as soon as the shaking ceases, and then continues to rise to a certain limiting value, which may be as much as ten times the initial current; if the liquid is kept continually agitated, a longer time is required for the current to increase to the limiting value.

By this method, if the duration of the current is sufficient to allow of the liberation from the cathode of more than about 0.24 gram of selenium per litre of water present, a deposit of red selenium begins to form at the bottom of the cell. If a solution prepared in this way is filtered and subjected to an *E.M.F.* of 40 volts between polished platinum electrodes, the current increases gradually from about 40 milli-amperes at the beginning to about 60 milli-amperes after two hours; if the current is interrupted for some time and then re-applied, the initial value is again about 40 milli-amperes, and the same gradual increase takes place. The increase of current seems to be due to a diminution in the resistance of the liquid present in the cell.

When a dilute solution of selenious anhydride is electrolysed with platinum electrodes, the phenomena observed vary with the *E.M.F.* employed. With 3 volts, a red deposit forms on the cathode, and the current gradually falls; with 17 volts, the deposit forms almost instantaneously and increases in thickness, the current remaining sensibly constant; whilst with 48 volts, the current gradually increases, whilst the liquid appears red in reflected and blue in transmitted light, a colloidal solution of selenium and a black cathodic deposit of selenium being formed.

The internal friction of such colloidal selenium solutions is sensibly identical with that of the distilled water from which they are prepared, the same being the case with solutions prepared by Gutlier's method (Abstr., 1902, ii, 652).
T. H. P.

Chemical Reactions in Gases Submitted to very High Pressures; Decomposition of Nitric Oxide; Formation of Nitrosyl Chloride. E. BRINER and A. WROCZYŃSKI (*Compt. rend.*, 1909, 149, 1372—1374. Compare Abstr., 1909, ii, 557).—Nitrosyl chloride is formed when a mixture of nitric oxide and hydrogen chloride is submitted to a pressure of 300 atmospheres. When nitric oxide is allowed to remain at high pressure in a sealed tube, it is colourless at first, but after a day appears bluish-green. If the tube contains a large quantity of the gas, drops of a blue liquid appear. The reaction is supposed to be represented by $6\text{NO} = 2\text{N}_2\text{O}_3 + \text{N}_2$; the synthesis of nitrosyl chloride would then be explained by the action $\text{N}_2\text{O}_3 + 2\text{HCl} = 2\text{NOCl} + \text{H}_2\text{O}$. No action occurs unless the nitric oxide is above a certain minimum pressure. In experiments in which the pressure in the tubes was gradually increased, the blue gaseous phase was first noticed at 28 atmospheres. The rate of formation of nitrosyl chloride increases with the pressure.
W. O. W.

A New Chloride of Phosphorus. ADOLPHE BESSON and A. FOURNIER (*Compt. rend.*, 1910, 150, 102—104).—On submitting a mixture of phosphorus trichloride and hydrogen to the action of an electric discharge (compare Abstr., 1909, ii, 663), a colourless liquid holding in suspension a yellow solid is produced. After filtration and purification by distillation under diminished pressure in an inert atmosphere, the liquid has a composition corresponding with that of phosphorus dichloride, P_2Cl_4 . It is a colourless, oily, and strongly fuming liquid. The fuming is not only caused by the action of moisture, but also by oxidation, and under certain conditions the liquid takes fire spontaneously. It has b. p. about $180^\circ/760$ mm. (decomp.), $95-96^\circ/20$ mm. without decomposition, m. p. -28° . It is decomposed by water with the formation of phosphorous acid and a yellow solid of indefinite composition. It decomposes slowly at the ordinary temperature and more quickly when heated to phosphorus trichloride and a yellow to red solid of indefinite composition, which is possibly a mixture of amorphous phosphorus with other chlorides.

Attempts to prepare phosphorus dibromide in a similar manner, and also by the action of hydrobromic acid on the dichloride, were not successful. A yellow to red solid of indefinite composition was obtained, which, in the light of the results obtained with the dichloride, may have resulted from the decomposition of a dibromide. T. S. P.

Phosphorus Suboxide. ALFRED STOCK (*Chem. Zeit.*, 1909, 33, 1354. Compare Burgess and Chapman, *Trans.*, 1901, 79, 1235).—Gutbier has stated (*Sitzungsber. physik.-med. Soc. Erlangen*, 1909, 40, 176) that the existence of phosphorus suboxide (P_2O) may be considered as proved by the work of Weidner (*Inaug. Diss.*, Erlangen, 1909), who has repeated Michaelis and Pitsch's experiments (Abstr., 1900, ii, 137) and found, in agreement with them, that the substance in question does not contain hydrogen which is attached to phosphorus, any hydrogen present being due to moisture. The author points out that Michaelis and Pitsch's experiments are not conclusive, and that Weidner has adduced no fresh experimental evidence in support of the existence of phosphorus suboxide. T. S. P.

Formula of Hypophosphoric Acid. I. and II. E. CORNEC (*Bull. Soc. chim.*, 1909, [iv], 5, 1081—1084, 1121—1126).—In the first paper the author reviews the evidence so far brought forward in favour of the simple, $H_2P_2O_6$, and double, $H_4P_2O_6$, formulae for this acid. It is pointed out that the five sodium salts prepared by Salzer (Abstr., 1886, 420) can all be regarded as derived from an acid represented by the simple formula, and that evidence furnished by (1) the decomposition of the salts by heat (Salzer and Joly), and (2) the electrical conductivity (Rosenheim, Stadler, and Jacobson, Abstr., 1906, ii, 744, and by Parravano and Marini, *ibid.*, 744, 848) is not conclusively in favour of either, although the latter, by analogy with the case of sodium pyrophosphate, to a certain extent supports the double formula. Ebullioscopic determinations of the molecular weight of the methyl ester are in favour of the simple formula (Rosenheim, Stadler and Jacobson, *loc. cit.*).

In the second paper, the author gives the results of measurements of the lowering of freezing point of solutions of hypophosphoric acid, its potassium salts, and of solutions of the acid progressively neutralised with potassium hydroxide, sodium hydroxide, or ammonia (Abstr., 1909, ii, 972). These all afford evidence in favour of the double formula, $H_4P_2O_6$, for this acid (compare Parravano and Marini, *loc. cit.*). The only valid argument for the simple formula, H_2PO_3 , still remaining is drawn from the esters of this acid, and these will now be further investigated.

T. A. H.

Extinction of Flames. WILLEM P. JORISSEN and N. H. SIEWERTSZ VAN REESEMA (*Chem. Weekblad*, 1909, 6, 1053—1062).—An investigation of the power of various gaseous mixtures to extinguish flame, and a review of previous work on this subject.

A. J. W.

Inner Cone of the Bunsen Flame. FRITZ HABER and BURRITT S. LACY (*Zeitsch. physikal. Chem.*, 1909, 68, 726—752).—The paper consists largely of a recapitulation and discussion of results already published by Haber's students and others (compare Haber and Richardt, Abstr., 1904, ii, 166; Davidson, Abstr., 1906, ii, 325; Tufts, *Physical Review*, 1906, 22, 193; Lacy, Abstr., 1908, ii, 1033). The experiments of Davidson and of Tufts on the electrical conductivity of flames have been repeated by Lacy, but are only briefly described, as Epstein and Krassa have since made extended observations by an improved method; the results of which are shortly to be published.

All the observations indicate that, with a plentiful supply of air, the electrical conductivity of the inner green zone of the Bunsen flame is relatively high, and much exceeds that in the neighbouring non-luminous regions. Further, the velocity with which the water equilibrium is established is much less outside than inside the luminous zone. Reasons are advanced in favour of the view that these two phenomena are connected, both being due to the influence of gas ions in the green luminous zone. In this case the ions are produced as a consequence of the chemical changes taking place in the luminous zone. The effect of ionisation in accelerating the establishment of equilibria has already been investigated for the carbon monoxide flame by Haber and Contes (compare Abstr., 1909, ii, 997).

G. S.

Nitrogen Compounds of Silicon. LUDWIG WEISS and THEODOR ENGELHARDT (*Zeitsch. anorg. Chem.*, 1909, 65, 38—104).—A review of previous work on the ill-characterised silicon nitrides is given. Pure silicon is best prepared by reducing potassium silicofluoride with massive aluminium, a better regulus being obtained than when aluminium powder is used. The regulus is crushed and extracted successively with hydrochloric, concentrated sulphuric, and hydrofluoric acids. The product, even after repeated boiling in a state of fine powder with hydrofluoric acid, contains 0.3—0.5% Fe, 0.1% Cu, and 0.72% SiO_2 . It forms brown, crystalline particles, D 2.30, and is not oxidised by oxygen at 700°.

Heated in pure nitrogen in a porcelain tube, combination begins near 1240°, the velocity of reaction increasing rapidly with the tempera-

ture. The product is amorphous and bulky, resembling cork, and is seen under the microscope to consist of several different substances. About 4% of the silicon volatilises, and forms a sublimate. The composition of the residue varies with the means of purification adopted. If boiled with potassium hydroxide solution, followed by hydrofluoric acid, a product having the formula Si_2N_3 is obtained, mixed with silica, which it is impossible to remove. If the free silicon is removed by boiling with a mixture of nitric and hydrofluoric acids, and the residue ignited and washed with hydrochloric acid, the compound SiN is obtained.

By heating silicon in nitrogen at $1300\text{--}1400^\circ$ until saturated, a nitride of the approximate formula Si_2N_4 is formed, and is only slightly decomposed by treatment with potassium hydroxide and hydrofluoric acid, or with a mixture of nitric and hydrofluoric acids.

The nitride SiN is white, and has $D\ 3.17$; the nitride Si_2N_3 has $D\ 3.64$, and the nitride Si_3N_4 , $D\ 3.44$, after allowing for the silica present. All the compounds are more or less decomposed by alkalis and by hydrofluoric acid.

Heating silicon in the flame of a coke fire gives a product containing carbon and nitrogen, corresponding approximately with the formula $\text{Si}_3\text{C}_2\text{N}$.

The estimation of nitrogen in the products is performed by heating with a mixture of equal parts of lead oxide, lead chromate, and lead peroxide in a porcelain tube in an atmosphere of carbon dioxide, increasing the temperature from 600 to 1000° . Kjeldahl's method gives less than half the total nitrogen. Silicon is estimated by fusion with potassium and sodium carbonates, as in the analysis of silicates. Commercial silicon is best analysed by fusion with potassium and sodium carbonates and potassium nitrate in a platinum crucible, which is first coated with a lining of the salt mixture before introducing the silicon. Any carborundum present is completely dissolved by these means.

C. H. D.

Action of Metals on Fused Sodium Hydroxide. I. MAX LE BLANC and L. BERGMANN (*Ber.*, 1909, 42, 4728—4747).—The action of various metals on fused sodium hydroxide at temperatures ranging between 400° and 720° has been investigated, all the experiments being carried out in an atmosphere of nitrogen. Preliminary experiments having shown that gold is the only metal which is not attacked by anhydrous, fused sodium hydroxide, the latter was always contained in a gold crucible, which was placed at the bottom of a silver tube surrounded by a porcelain tube. This tube could be heated to any desired temperature by an appropriate furnace arrangement. Pure dry nitrogen was passed through the reaction tube, and the extent of any reaction taking place was measured by determining the amount of water and hydrogen present in the issuing gas.

Sodium hydroxide can be readily dehydrated at a temperature of 400° , and undergoes no further loss in weight on heating to 720° , so that a dissociation corresponding with the equation: $2\text{NaOH} = \text{Na}_2\text{O} + \text{H}_2\text{O}$ does not take place between these temperatures.

Silver and sodium react with fused sodium hydroxide under

evolution of hydrogen; platinum, copper, iron, nickel, aluminium, zinc, and magnesium cause an evolution of hydrogen, and at the same time water is eliminated. The simplest explanation of this double reaction is that the compound $M(\text{ONa})_x$, which is formed according to the equation: $M + x\text{NaOH} = M(\text{ONa})_x + x\text{H}$, where M is a metal, forms a more or less complex compound with Na_2O , resulting from the loss of water from two molecules of the sodium hydroxide.

The valencies of the metals were calculated from the amount of hydrogen evolved, and found to be normal in the case of sodium, magnesium, copper, iron, aluminium, and zinc. Silver, nickel, and platinum gave abnormal values, as, for example, trivalent silver.

When the gold crucible containing sodium hydroxide and copper turnings was heated at 700° , it absorbed a not inconsiderable quantity of copper, forming an alloy. This alloy is not formed at this temperature in the absence of sodium hydroxide. When silver was used in place of copper, the silver became alloyed, and at the same time the silver tube containing the gold crucible took up some of the gold. The latter phenomenon was also noticed with nickel, but with none of the other metals. Magnesium also formed a gold-magnesium alloy.

T. S. P.

Alkali Hydrogen Carbonates. ROBERT DE FORCRAND (*Compt. rend.*, 1909, 149, 825—829).—Hydrogen carbonates of the formula $\text{R}_2\text{CO}_3 \cdot 2\text{RHCO}_3 \cdot x\text{H}_2\text{O}$, such as natural trona, have only occasionally been obtained in the laboratory. Dry potassium carbonate when left exposed to the air attains the composition $\text{K}_2\text{CO}_3 \cdot 2\text{KHCO}_3$.

When dilute solutions of potassium, rubidium, and cesium carbonates are exposed at room temperature for several weeks, carbon dioxide is absorbed until the composition corresponds with the formulae: $8\text{K}_2\text{CO}_3 \cdot 2\text{KHCO}_3$; $3\text{Rb}_2\text{CO}_3 \cdot 2\text{RbHCO}_3$, and $4\text{Cs}_2\text{CO}_3 \cdot 2\text{CsHCO}_3$.

Although the amount of carbonic acid absorbed depends on the dilution, temperature, and pressure of carbon dioxide in the air, the results are held to indicate the formation of definite compounds. When solutions of hydrogen carbonates are boiled for prolonged periods, they are found to contain hydrogen carbonates of the same composition as the above, but the crystals deposited on evaporation have the composition: $5(\text{K}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}) \cdot 4\text{KHCO}_3$;

$3(\text{Rb}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}) \cdot 2\text{RbHCO}_3$;

$5(\text{Cs}_2\text{CO}_3 \cdot 3\frac{1}{2}\text{H}_2\text{O}) \cdot 2\text{CsHCO}_3$. The last is converted on the water-bath into $5(\text{Cs}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}) \cdot 2\text{CsHCO}_3$.

The heats of formation of these hydrogen carbonates are negative and small in value.

R. J. C.

Hydrates of Rubidium and Cesium Hydroxides. ROBERT DE FORCRAND (*Compt. rend.*, 1909, 149, 1311—1344. Compare Abstr., 1906, ii, 445).—When an aqueous solution of rubidium hydroxide is allowed to evaporate at 15° , crystals of the hydrate $\text{RbOH} \cdot 2\text{H}_2\text{O}$ are deposited; these have m. p. $45\text{--}46^\circ$, and heat of solution -0.646 Cal. at 15° . The thermal properties of rubidium hydroxide and its hydrates are closely analogous with those of the corresponding potassium compounds.

The monohydrate of caesium hydroxide already studied (*loc. cit.*) is more stable than those of the rubidium and potassium hydroxides. Although thermochemical measurements indicate the probable existence of a dihydrate, this has not yet been isolated, the crystals deposited when a solution of caesium hydroxide is allowed to evaporate being those of the monohydrate contaminated by mother liquor.

A saturated solution of rubidium hydroxide at 15° contains 64.17% of RbOH, whilst a saturated solution of the caesium compound contains 79.41% of CsOH.

W. O. W.

Acid Sulphates. V. JOH. D'ANS (*Zeitsch. anorg. Chem.*, 1909, 65, 228—230. Compare Abstr., 1909, ii, 885).—Determinations of the solubility of ammonium sulphate in mixtures of sulphuric acid and water at 25° indicate the separation of three solid phases: ammonium sulphate, and the acid salts $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ and NH_4HSO_4 . The composition of the second salt was confirmed by isolation and titration. Washing with alcohol or ether is impracticable, on account of decomposition of the salt, and mechanical separation of the acid must therefore be employed.

Unlike sodium and potassium sulphates, the solubility of which increases with increasing sulphuric acid concentration, that of ammonium sulphate falls to a minimum, and then rises only very slightly to the limiting solution: $(\text{NH}_4)_3\text{SO}_4 - (\text{NH}_4)_4\text{H}(\text{SO}_4)_2$. The curve for $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ also has a minimum.

C. H. D.

Action of Heat and Light on Silver Sulphite and its Alkali Double Sulphites. Amount of Dithionate Obtained. HENRI BAUBIGNY (*Compt. rend.*, 1909, 149, 858—860. Compare Abstr., 1909, ii, 1004).—Analysis of the products obtained by decomposing silver sulphite under various conditions shows that as much as 89.84% may be converted into dithionate, whilst the remainder is converted into sulphate. Sodium silver sulphite may give as much as 97.5% of sodium dithionate.

Silver sulphite is perfectly stable in the dark, but in diffused light it is slowly decomposed, giving dithionate and a small proportion of sulphate.

R. J. C.

Necessity for Exactness in Describing Reactions. [Action of Heat on Sulphites.] HENRI BAUBIGNY (*Compt. rend.*, 1909, 149, 1378).—Polemical against Colson (compare this vol., ii, 34), pointing out that nowhere in the literature is there the statement, ascribed by Colson to Berthier, that the double sulphites of the alkali metals and of silver decompose with the formation of sulphate.

T. S. P.

New Preparation of the Second Anhydrous Modification of Calcium Sulphate. PAUL ROHLAND (*Zeitsch. anorg. Chem.*, 1909, 65, 105—107).—When either gypsum or the hemihydrate is dissolved in hot concentrated sulphuric acid, an anhydrous salt separates on cooling, which proves to be the second anhydrous calcium sulphate, known as Estrich gypsum. There are, in addition to the naturally occurring anhydrite, four anhydrous modifications of calcium sulphate.

(1) Kraut's anhydride, obtained at 100°; (2) van't Hoff's anhydride, also prepared at 100°, and hydrating very rapidly; (3) dead-burnt gypsum, prepared above 130°, incapable of hardening; (4) a modification prepared by heating above 530°, or by the action of sulphuric acid, hydrating very slowly. C. H. D.

Decomposition of Calcium Carbonate. ERNST H. RIESENFELD (*J. Chim. phys.*, 1909, 7, 561—569).—New measurements of the dissociation pressure of calcium carbonate have been made with the object of explaining the discrepant results obtained by Brill (compare Abstr., 1905, ii, 522). The following values are recorded in mm. of mercury: 700°, 50; 750°, 99; 800°, 195; 850°, 370; 900°, 700. These data are in good agreement with the thermodynamic equation of Nernst, and by means of this equation the dissociation pressures are calculated for every 100° between 600° and 1500°. H. M. D.

Solubility of Cadmium Sulphide in Light Petroleum Containing Oil. G. C. A. VAN DORP and J. RODENBURG (*Chem. Weekblad*, 1909, 6, 1038).—A colloidal solution of cadmium sulphide is obtained by triturating this substance with oil and adding light petroleum.

A. J. W.

[Formation of Alloys by Pressure.] WALTHER SPRING (*Zeitsch. Elektrochem.*, 1909, 15, 984).—The author agrees with Tammann's view (Abstr., 1909, ii, 669) that the formation of alloys under pressure is a result of diffusion, which is not accelerated by the pressure. T. E.

Constitution and Heat Contents of Lead-Tin Alloys. W. GUERTLER (*Zeitsch. Elektrochem.*, 1909, 15, 953—965).—The recent investigations of Rosenhain and Tucker (Abstr., 1908, ii, 1038) and of Degens (Abstr., 1909, ii, 888) leave the question of the cause of the development of heat at about 150° undecided; it may be due to decomposition of mixed crystals of lead and tin (Guertler, Abstr., 1909, ii, 319), or to the formation of a compound of about the composition Sn_3Pb_4 . Using measurements of the quantity of heat given out by mixtures of lead and tin in cooling from 380° to 100° made by Spring in 1886, and the melting-point curve determined by Rosenhain and Tucker and Degens, the author has calculated the heats of fusion of different alloys of tin and lead. The values obtained are very much larger than those calculated on the assumption that the heat of fusion of the alloy is the mean of the heats of fusion of its constituents. This shows that liquid tin and lead must give out a considerable quantity of heat when they are mixed together. T. E.

Peroxidised Compounds. LUIGI MARINO (*Zeitsch. anorg. Chem.*, 1909, 65, 25—31).—The isolation of a salt, $\text{Pb}_2\text{Se}_2\text{O}_7$ (Abstr., 1909, ii, 575), proved lead sesquioxide to be a true feebly-basic oxide, and not a salt of the dioxide. In the attempt to prepare other sesquioxides, the liquid obtained by the addition of an acid solution

of potassium permanganate to a mixture of hydrogen peroxide and sulphuric acid at -15° , supposed by Berthelot to contain the compound H_2O_8 , has been examined.

The solution is capable of oxidising sulphurous acid completely to sulphuric acid. It is probable that the compound present is a higher acid of manganese, as the curve connecting volume of oxygen evolved, in the absence of sulphurous acid, with time has exactly the same form as that obtained with a mixture of chromic acid and hydrogen peroxide, in which perchromic acid is known to be present. It is shown that the oxidation of the sulphurous acid is not due to the action of free oxygen in supersaturated solution. C. H. D.

Relation of Thallium to the Alkali Metals: a Study of Thallium Zinc Sulphate and Selenate. ALFRED E. H. TUTTON (*Proc. Roy. Soc.*, 1910, 83, 4, 211–226).—A detailed crystallographic examination of the double salts: $\text{Tl}_2\text{SO}_4 \cdot \text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{Tl}_2\text{SeO}_4 \cdot \text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$ has been made.

The various crystallographic data and the morphological angles are tabulated. The double sulphate was found to have $D \ 3 \cdot 7204$ by the author's pycnometer method; consistent results could not be obtained for the double selenate.

From a comparison of the thallium salts with the corresponding potassium, rubidium, ammonium, and caesium salts, the author concludes that the morphological and physical properties of the crystals of the thallium double salts are such as quite entitle them to places in this isomorphous series, but not to places in the more exclusive eutropic series obeying the law of progression according to the atomic weight of the interchangeable metals.

The position of thallium in either the simple or double salt series is very close to that of ammonium, and therefore also to that of rubidium. This does not hold, however, for the refractive power. In respect of this property, the thallium double salts are quite exceptional, in that they exhibit abnormally high refraction, and a larger amount of dispersion and of double refraction. The mean refractive index of thallium zinc sulphate for sodium light is 1.6064, whereas the values for the other four double sulphates range from 1.4859 to 1.5054. H. M. D.

Acid Sulphates. VI. JOH. D'ANS and O. FRITSCHÉ (*Zeitsch. anorg. Chem.*, 1909, 65, 231–232. Compare this vol., ii, 125).—Thallium sulphate and dilute sulphuric acid form two acid salts, $\text{Tl}_2\text{H}(\text{SO}_4)_2$ and THSO_4 , the limits of existence of which at 25° have been determined. The curves differ from those of the alkali sulphates, the solubility increasing almost continuously with the sulphuric acid concentration. C. H. D.

The System Mercuric Chloride and Mercurous Chloride. W. P. A. JONKER (*Chem. Weekblad*, 1909, 6, 1035–1038).—Mercuric chloride has m. p. 277° and b. p. 301° . Addition of mercurous chloride lowers the m. p. to the eutectic point 271° . A saturated solution of mercurous chloride in mercuric chloride contains 12% of the former, and has b. p. 304° . Mercurous chloride sublimes at 373° . A. J. W.

Resolution of Ytterbium. CARL AUER VON WELSBACH (*Monatsh.*, 1909, 30, 695—700 + i—vi).—Polemical (compare Welsbach, *Abstr.*, 1908, ii, 591). Disputes Urbain's claim of priority (compare *Abstr.*, 1907, ii, 956; 1908, ii, 849).
E. F. A.

Electrical Properties of Aluminium Copper Alloys. WIZOON BRONIEWSKI (*Compt. rend.*, 1909, 149, 853—855. Compare Pushin, *Abstr.*, 1907, ii, 774).—Determinations were made of the electrical conductivity, temperature-coefficient of resistance, solution potential, and thermoelectric power of a complete series of alloys of copper and aluminium. Alloys containing more than 12% of either metal, which are very brittle, had not been investigated previously. The electrical properties in question were often greatly modified by annealing, but the inferences drawn from the curves of both tempered and annealed alloys are the same. The annealing was carried out in an electric furnace for four to five hours at a temperature somewhat below the solidus of each alloy.

The curves indicate the compounds Al_2Cu , AlCu , Al_3Cu_3 , AlCu_2 . The compound Al_3Cu_3 has not been detected previously, but the other three were found by Le Chatelier and by Guillet (*Abstr.*, 1905, ii, 712). Carpenter and Edwards (1907) found no evidence for the compound AlCu , but, on the other hand, their compound AlCu_4 could not be detected by the author.

The compound AlCu_2 is depolymerised above 500° , when the larger crystals are split up into finely crystalline masses, and the electrical resistance is doubled.
R. J. C.

Crystalline Structure of Iron at High Temperatures. WALTER ROSENHAIN and J. C. W. HUMFREY (*Proc. Roy. Soc.*, 1910, 83, 4, 200—209).—The structural changes which accompany the deformation of iron at high temperatures have been investigated. The material employed for most of the experiments was a pure form of commercial iron of very low carbon content. To remove oxygen, the metal was heated to about 900° in a current of pure dry hydrogen. A strip of this iron, the surface of which had been polished previously, was then placed in a specially designed piece of apparatus, in which it could be electrically heated in a vacuum and subjected to stress whilst at a high temperature. By means of comparative observations on specimens which were heated without straining, the changes in the structure which resulted from the rise of temperature could be distinguished from those which were a consequence of the applied stress.

Under the conditions of the experiments, the strips of metal were not uniformly heated, and whereas the temperature of the central portion exceeded 1000° , the metal at and near the ends did not reach a visible red heat. Corresponding with the distribution of temperature, the micro-structure exhibits three distinct regions when the strips are examined from the central portion towards either end.

The structural differences lead to the conclusion that pure iron between the ordinary temperature and 1000° exists in three distinct modifications possessing widely different mechanical properties. The temperature ranges in which these modifications exist are consistent with

the view that they are identical with the α -, β -, and γ -forms of Osmond and Roberts-Austen, as indicated by cooling curves. The deformation observations also indicate that β -iron, although existing at a higher temperature, is harder and stronger than α -iron, and that the reversible transformation of these forms is accompanied by a change of volume. The γ -iron obtained in the case of approximately pure iron exhibits the structure and properties of the " γ -iron" alloy steels.

II. M. D.

Passivity of Iron. P. KRASSA (*Zeitsch. Elektrochem.*, 1909, 15, 981—984).—A reply to Müller and Königsberger (Abstr., 1909, ii, 1016). The author maintains his former criticism (Abstr., 1909, ii, 738), and insists further that the potentials of Müller and Königsberger's mirrors were so abnormal that their behaviour cannot be regarded as proving anything about ordinary iron. T. E.

Retardation of the Oxidation of Iron by Chromic Chloride. PAUL ROHLAND (*Zeitsch. Elektrochem.*, 1905, 15, 865—866).—Chromic chloride retards the oxidation of iron; an increase of the concentration of the hydrogen ions in the solution causes the protection to disappear. The action persists in presence of chlorine ions, and to a less extent in presence of bromine ions. Ferric chloride is, however, an exception; possibly the hydrogen ions formed by hydrolysis account for this. Chromic ions protect iron in presence of sulphates, but not in presence of nitrates. T. E.

Carbon Monoxide in Steels. E. GOUTAL (*Compt. rend.*, 1909, 149, 1129—1131).—The author has shown previously (Abstr., 1909, ii, 519) that when steels are dissolved in solutions of copper salts, gases are evolved which contain carbon dioxide and monoxide. The percentage of carbon monoxide was estimated by making use of the oxidising action of iodine pentoxide at 75°, and found to have a mean value of 0.014%. These results are now confirmed as follows. The evolved gases were swept by a current of nitrogen through a series of tubes, each containing 25 c.c. of a 1% solution of delibinated guinea-pig's blood. Each tube could absorb a known quantity of carbon monoxide, and by determining the number of tubes which showed the characteristic absorption spectrum of carbon monoxide-haemoglobin, the percentage of carbon monoxide could be found.

The percentages thus determined are independent of: (1) the amount of steel taken; (2) the duration of the experiment; (3) the acidity of the copper solution used; (4) the substitution of cupric chloride by a solution of iodine in potassium iodide; (5) the gas (air or nitrogen) employed for sweeping out the evolved gases.

Analyses of different steels show that the percentage of carbon monoxide does not appreciably exceed 0.014. This percentage (0.014) remains approximately constant for ordinary steels containing more than 0.3% of carbon. Nickel steels contain a much less, and chromium steels about the same, percentage of carbon monoxide as ordinary steels of the same carbon content.

Samples of steel were taken from a Siemens Martin furnace one

hour and then forty-five minutes before tapping, and also just before and just after the addition of ferro-manganese. The percentage of carbon monoxide remains practically constant during the period of decarburisation; it then falls considerably just before the addition of ferro-manganese, to rise to its final value after the ferro-manganese has been added. This is true for both soft and hard steels, in which the percentages of carbon monoxide are respectively 0.0063 and 0.0137. T. S. P.

Oxygen Evolved from Ferric Oxide at High Temperatures. SIEGFRIED HILFERT (*Ber.*, 1909, 42, 4893—4895).—In contradistinction to Walden (*Abstr.*, 1908, ii, 852), the author has not been able to determine the temperature at which the pressure of oxygen over ferric oxide is equal to that of the atmosphere. The results vary considerably with the method of preparation and previous treatment of the ferric oxide, and the velocity with which equilibrium is attained is extremely slow. In general, the amount of ferrous oxide formed by heating ferric oxide in the air to 1300° did not exceed 5°; only above 1350° was there further loss of oxygen. In one experiment, heating the ferric oxide to 1600° only increased the percentage of ferrous oxide from 2.95 to 3.1%.

It is pointed out that thermodynamical calculations according to Nernst's theorem are totally untrustworthy when the dissociation of such substances as ferric oxide is taken as the basis. T. S. P.

Phosphorus Compounds of Iron. N. S. KONSTANINOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1220—1240).—The alloys of phosphorus and iron were divided by Stead (*J. Iron and Steel Inst.*, 1900, 58, 60) into five classes: (1) those containing 0—1.7% of phosphorus and consisting of solid solutions of Fe_3P in iron; (2) alloys with 1.7—10.2% of phosphorus, which form solid solutions of Fe_3P in iron and give a eutectic alloy (10.2% P) consisting of a definite solid solution and the phosphide Fe_3P ; (3) those with 10.2—15.58% P, also consisting of the eutectic and Fe_3P , the m. p. of the latter (15.58% P) being 1060°; (4) alloys containing 15.58—21.6% P and consisting of Fe_3P and Fe_2P ; (5) those with more than 21.6% P and containing Fe_2P and another phosphide richer in phosphorus. These results were confirmed by Saklatwalla (*J. Iron and Steel Inst.*, 1908, 77, 92—103), who gave a melting-point diagram for these alloys.

The author's investigations of iron-phosphorus alloys containing up to 21.0% (32.4 atom.%) of phosphorus show that the solidification-point diagram consists of three branches: (1) *AB*, falling from 1514°, the m. p. of iron, to 1020°, corresponding with 10.2% Fe; (2) *BC*, rising continuously from *B* to *C*, and corresponding with the separation of crystals of the phosphide Fe_3P . The separate solidification curves exhibit two halts, one showing a regular rise corresponding with the separation of crystals of the phosphide, and the other at a constant temperature corresponding with separation of the eutectic and gradually diminishing in magnitude as *C* is approached. Micrographic examination of these alloys shows the presence of rhomboidal plates of Fe_3P surrounded by the eutectic; (3) *CD*, rising at first rapidly and

afterwards more slowly to the point *D*, corresponding with the phosphide Fe_3P (compare Gercke, Abstr., 1908, ii, 1041; Le Chatelier and Wologdine, Abstr., 1909, ii, 1017).

A list is given of the known phosphides, arsenides, and antimonides of the metals of the iron series of the eighth group in the periodic system.⁴⁷ With the typical metals of this series, iron, cobalt, and nickel, these compounds are more varied in type than with the initial members, manganese and copper. With the metals of the other groups of the periodic system, these compounds are, in the great majority of cases, derived from the hydrogen phosphides PH_3 and PH_4 . With phosphorus, the most stable compounds are those rich in metal, such as M_3P , whilst with arsenic and especially with antimony, compounds relatively poor in metal, such as MSb_3 , are the most stable.

T. H. P.

Iron Phosphides. OTTO KUHN (*Chem. Zeit.*, 1910, 34, 45—46).—Le Chatelier and Wologdine (Abstr., 1909, ii, 1017) state that there are only four iron phosphides, namely, Fe_3P , Fe_2P , FeP , and Fe_5P_3 , and, further, that the existence of the last two has not been proved with absolute certainty. In the course of an investigation on the preparation of copper phosphide by heating a mixture of bone ash, powdered quartz, wood-charcoal, and granulated copper, the author obtained a product which, on solution in nitric acid, left a small residue of glistening needles, which were practically insoluble in hot or cold concentrated nitric acid or in dilute sulphuric acid, although readily soluble in aqua regia. The results of analysis agree approximately with the formula Fe_3P_2 , the iron coming from the impure quartz used in the preparation. These needles cannot be considered as a solid solution of Fe_3P and Fe_2P , since the former compound is readily soluble in nitric acid.

T. S. P.

Electromotive Forces of Cobalt Alloys. F. DUCELLEZ (*Compt. rend.*, 1910, 150, 98—101. Compare Pushin, Abstr., 1907, ii, 325, 618, 774, 837).—From the curves showing the relation between the composition of the alloy and the potential with respect to a normal solution of cobalt sulphate, the existence of the following compounds has been deduced: CoSn , CoSb , CoSh_2 . Alloys of cobalt and bismuth form two phases, the one rich in cobalt, and the other and heavier, rich in bismuth. Bismuth lowers the melting point of the cobalt which, when liquid, is capable of dissolving some bismuth. From liquid alloys containing 0—94 (approx.) % Bi, the cobalt separates in a pure state on cooling. The results obtained with lead and cobalt are similar to those with bismuth and cobalt. Cobalt and copper do not form compounds with each other, but give either homogeneous solid solutions or two phase systems of solid solutions.

T. S. P.

Absorption of Carbon by Metals, Especially Nickel, in the Electrolysis of Aqueous Solutions. GUSTAV LAMBERS (*Zeitsch. Elektrochem.*, 1909, 15, 973—981).—The nickel which is deposited from a solution containing ammonium oxalate contains up to 4% of carbon; the smaller the quantity of nickel deposited and the larger

the quantity of ammonium oxalate used, the greater is the quantity of carbon in the deposit. The carbonaceous residue obtained by dissolving the nickel by copper chloride and chlorine contained ammonium chloride, which could not be completely removed. The percentage of carbon in the residue increased as greater precautions were taken to free it from ammonium salts. The ammonium salts of glycollic, formic, and acetic acids also yield nickel containing carbon, but if a diaphragm is interposed between the anode and cathode, carbon-free nickel is obtained if the cathode solution contains free ammonia, but not if it is kept slightly acid. Carbon dioxide also gives carbonaceous nickel (from nickel ammonium sulphate solution), but in presence of a little free ammonia, carbon-free metal is obtained. Since the metal obtained from ammonium oxalate solution contains carbon even in presence of a large excess of free ammonia, the anodic carbon dioxide cannot be the source of the carbon. The same applies to carbon monoxide, which behaves in the same way as carbon dioxide. Methane, ethane, and ethylene give carbon-free nickel, but acetylene, passed into the cathode solution, gives carbonaceous nickel both in neutral and strongly ammoniacal solutions.

It is shown that acetylene is formed in small quantities at the cathode when ammonium oxalate is electrolysed with platinum and nickel cathodes, but not with iron, copper, or tin; some ethane is also formed by further reduction of the acetylene.

The carbon is contained in the nickel in the form of a carbide; when the metal is dissolved in hydrochloric acid, the whole of the carbon is evolved in the form of hydrocarbons.

Iron, at which no acetylene is formed, is deposited from ammonium oxalate solutions quite free from carbon. It appears, therefore, quite clear that the carbon is contained in the nickel as carbide, formed from acetylene during the deposition of the nickel.

T. E.

Alloys of Nickel and Copper. ÉMILE VIGOUROUX (*Compt. rend.*, 1909, 149, 1378—1380. Compare Kurnakoff, *Abstr.*, 1907, ii, 525; Guertler, *Abstr.*, 1908, ii, 557).—From an examination of the action of acids on alloys of copper and nickel, and by determinations of the *E.M.F.* produced in cells when one of the metals constitutes one of the electrodes and an alloy of the two the second electrode, the author is led to the conclusion that no definite compounds of nickel and copper exist.

W. O. W.

Two New Nickel Phosphides. PIERRE JOLIBOIS (*Compt. rend.*, 1910, 150, 106—108).—Twenty-one grams of an alloy of tin and nickel containing 5% of nickel were heated with 1—4 grams of phosphorus in a vacuum sealed tube to 700°. On cooling and dissolving the lower part of the ingot obtained in warm concentrated hydrochloric acid, small, prismatic crystals of metallic appearance were left, having a composition corresponding with the formula NiP_2 , and $D^{18} = 4.62$. They are soluble in nitric acid, decomposed by fused sodium hydroxide, and lose their phosphorus at 650°.

If the proportion of phosphorus in the reaction mixture is increased to 7—10 grams, hydrochloric acid leaves a mixture of tin phosphide

(SnP_2) with another nickel phosphide, having the formula NiP_3 . These are separated by heating the mixture in a vacuum to 360° , whereby the compound SnP_3 loses phosphorus, giving the compound SnP_2 (compare Abstr., 1909, ii, 319), which is then readily soluble in hydrochloric acid. This second phosphide of nickel forms microscopic crystals of metallic appearance, which are readily soluble in nitric acid, and is decomposed, with incandescence, by fused sodium hydroxide; the phosphorus is lost at 580° ; $D^{18} = 4.19$.

T. S. P.

Mixed Halogen Compounds of Tin. VICTOR AUGER (*Compt. rend.*, 1909, 149, 860—862).—Numerous compounds of the types: SnCl_2Br , SnCl_2Br_2 , SnClBr_3 have been described, all of which are said to decompose on distillation into the simple stannic salts: SnX_4 , SnY_4 .

The author shows that mixtures of SnBr_4 and SnI_4 give a normal freezing-point curve with a eutectic at the composition $\text{SnBr}_{2.3}\text{I}_{0.8}$. The supposed compound, SnBr_2I_2 , melting at 54° is identical with an equimolecular mixture of SnBr_4 and SnI_4 , and may be separated by a series of ten fractional crystallisations into fractions melting at 88° and 27° , of compositions $\text{SnBr}_{1.2}\text{I}_{2.8}$ and $\text{SnBr}_{2.7}\text{I}_{1.3}$ respectively. Similarly, the supposed compounds SnBrI_3 (m. p. 103°) and SnBr_3I may be partly resolved by crystallisation.

The cooling curve of SnBr_2I_2 from 55° is an unbroken line, such as is given by a mixture, although the crystals are brilliant and apparently homogeneous. The author suggests that in all molten mixtures of the composition $\text{SnBr}_x\text{I}_{4-x}$, the halogen atoms are perfectly mobile. The same is suggested for the chlorobromides and iodochlorides.

R. J. C.

Natural Zirconium Dioxide. LUDWIG WEISS [and, in part, RICHARD LEHMANN] (*Zeitsch. anorg. Chem.*, 1909, 65, 178—227).—Native zirconium dioxide, baddeleyite, instead of being isomorphous with rutile and cassiterite, is monoclinic. If artificially crystallised from borax, however, it is quadratic, and isomorphous with rutile. Several hundred kilograms of the native mineral from Brazil have been used for the investigation. It contains 88.09% ZrO_2 , 7.39% SiO_2 , 0.74% TiO_2 , and 3.78% Fe_2O_3 . About one-half of the impurities may be removed by boiling with hydrochloric acid, and rather more by heating with sodium sulphate, salt, and carbon. Pure zirconia is obtained by heating the mineral with potassium hydrogen fluoride, and crystallising the double fluoride.

For analysis, the mineral is fused with sodium hydrogen sulphate. Iron is separated, with aluminium if present in small quantity, by precipitation with ammonium sulphide from a hot solution containing ammonium oxalate and tartrate. After removal of organic salts from the filtrate, the zirconium hydroxide is precipitated with sodium hydroxide and hydrogen peroxide, titanium being left in solution. The following analyses represent dense fragments:

	ZrO_2	Fe_2O_3	Al_2O_3	TiO_2	SiO_2	H_2O	Total.
I.	92.07	2.73	1.17	trace	2.73	0.88	99.58
II.	84.96	7.01	3.99	trace	1.37	1.04	98.37

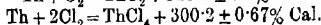
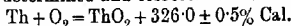
VOL. XXVIII. ii.

Pure zirconia is obtained by a long process, which is described in detail. Repeated fractionation does not produce any indication of a separation of the zirconium into two constituents. Small quantities of rare earths have been recognised spectroscopically, but scandium is present only in faint traces.

The specific gravity varies, even of pure samples, and is apparently dependent on the extent of the previous heating. After compressing to form rods under a pressure of 8000 kilograms per sq. cm., it may be fused by a powerful arc, using 500 amperes or more, and then has D_{25}^{20} 5.48. The linear coefficient of expansion is $\alpha = 0.00000084$, very near to that of fused quartz. Crucibles, etc., may be made by mixing the zirconia with 10% of magnesia, or clay. Platinum may be rendered completely liquid by heating in a zirconia crucible with an oxy-hydrogen flame. Quartz may also be melted without destruction of the crucible. Other technical applications are described.

C. H. D.

Thorium. H. VON WARTENBERG (*Zeitsch. Elektrochem.*, 1909, 15, 866—872).—Thorium is prepared by electrolysis of thorium chloride dissolved in a mixture of fused potassium and sodium chlorides (Abstr., 1906, ii, 678). The action of the electrolyte on the porcelain crucible is avoided to a great extent by using a graphite crucible which fits closely into the porcelain crucible, both as anode and as containing vessel for the fused salts. The cathode is a graphite rod, and the electrolysis is carried out as rapidly as possible in an atmosphere of nitrogen. The metal is obtained in the form of crystals mixed with carbon, from which it is separated by means of methylene iodide. Careful analyses gave 87.6 to 88.9% thorium, 0.06% iron, 0.04% sodium, 0.03% silicon, and 0.15% carbon (mechanically admixed). The remainder was oxide. Microscopic examination showed this to be mixed with the metal; it is left in the form of a felted mass when the metal is dissolved in acid. Experiments with mixtures of lead and thallium with their oxides show that mechanically-admixed oxides do not affect the ductility of these soft metals very seriously, so that the ductility of thorium cannot be used as an argument in favour of its purity (Abstr., 1909, ii, 53). The heats of formation of thorium oxide and chloride were determined and corrected for the impurities present:



The results are given in kilogram calories.

The metal melted at 1700° , but the carbon in it combined with it, forming about 2% of carbide, which would lower the melting point very considerably. Thorium sulphide has been prepared, and its formula is shown to be ThS_2 .

T. R.

The Atomic Weight of Vanadium. WILHELM PRANDTL and BENNO BLEYER (*Zeitsch. anorg. Chem.*, 1909, 65, 152—165).—Vanadium oxy-trichloride, VOCl_3 , is the only vanadium compound capable of being obtained in a state of sufficient purity for atomic weight determinations. Ammonium metavanadate is three times precipitated from its boiling solution with ammonium chloride, ignited,

heated with hydrofluoric acid, and then mixed with carbon and ignited, first in a current of hydrogen and then in one of chlorine. The product is fractionally distilled, and then has b. p. $124.4^{\circ}/733$ mm. (corr.). When no longer changed by further fractionation, it has $D_4^{15.5}$ 1.8362. The vapour density proves it to be undecomposed.

The liquid is distilled into glass bulbs and weighed; the bulbs are broken in glass flasks containing water and zinc. After acidifying with nitric acid and filtering, the chlorine is precipitated with silver nitrate. The mean result of nine determinations obtained is $V = 51.0$ ($Ag = 107.880$; $Cl = 35.460$), which is lower than the previously accepted value, 51.2. The difference is explained by a criticism of Roscoe's method.

C. H. D.

Solution of Platinum in Sulphuric Acid and the Products of Reaction. MARCEL DELÉPINE (*Compt. rend.*, 1910, 150, 104—106).—Quennessen (*Abstr.*, 1906, ii, 551) has attributed the solvent action of sulphuric acid on platinum to the intermediate action of oxygen of the air. The author shows that all Quennessen's results can be explained by assuming that the reaction, as represented by the equation $2Pt + 7H_2SO_4 \rightleftharpoons 2OH \cdot Pt(SO_4H)_2 + 3SO_2 + 4H_2O$, is reversible. Sulphuric acid and spongy platinum were boiled up together in a flask, while various gases were passed through the liquid. With carbon dioxide, the reaction proceeded according to the above equation. When air was used, twice as much platinum dissolved, and less sulphur dioxide was evolved, owing to the oxidation of the sulphur dioxide to trioxide under the influence of the platinum. With oxygen, four times as much platinum dissolved, and less still sulphur dioxide was evolved. When a mixture of carbon and sulphur dioxides was used, no solution of platinum took place, and, in some cases, platinum was precipitated from solution.

The compound of platinum mentioned above can be isolated in the form of the potassium salt, $OH \cdot Pt(SO_4H)_2 \cdot SO_4K$, by adding a dilute solution of a potassium salt to the orange-yellow liquid. If the platinum is boiled with sulphuric acid for a long time, the liquid becomes darker and darker in colour, finally almost black, and after thirty hours may contain more than 20 grams of platinum per litre. From this solution a brown compound can be obtained, having the formula $Pt(OH)_2 \cdot SO_4H_2 \cdot H_2O$, and crystallising in rectangular prisms, which are very soluble in water, concentrated sulphuric acid, alcohol and acetone. At 100° it loses $1.5H_2O$. The compounds can also be obtained by the oxidation of platinum dioxide with nitric acid.

T. S. P.

Mineralogical Chemistry.

Volcanic Gases. ALBERT BRUN (*Bull. Soc. chim.*, 1910, [iv], 7, 4).—It is pointed out that the use of the word "fumarole" in Gautier's e-statement (*Bull. Soc. chim.*, 1909, [iv], 5, 982; compare *Abstr.*,

1909, ii, 744, 745) of the author's argument in favour of the view that aqueous vapour is of little importance in volcanic explosions (Abstr., 1907, ii, 33), is confusing. T. A. H.

Gas from Thermal Springs: Presence of Krypton and Xenon. CHARLES MOUREU and A. LEPAPE (*Compt. rend.*, 1909, 149, 1171—1174).—The authors have recognised the presence of krypton and xenon in twenty-six French thermal springs. The fact was established that the gases did not come from the atmosphere in the vicinity of the springs. W. O. W.

Dawsonite, a Sodium-Aluminium Carbonate. RICHARD P. D. GRAHAM (*Trans. Roy. Soc. Canada*, [iii], 2, iv, 165—177).—This mineral is found in two dykes in Montreal, at Ténés, Algeria, and in Tuscany. Terminated crystals are very rare, but the author found a few belonging to the orthorhombic, holosymmetric class [$a:b:c=0.6475:1:0.5339$]. The optical properties were studied. Some very pure crystals on analysis gave

Al_2O_3	Na_2O	CaO	MgO	CO_2	H_2O
35.70	21.62	1.59	trace	31.56	11.51

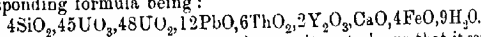
agreeing with the formula $Al_2O_3 \cdot Na_2O \cdot 2CO_2 \cdot 2H_2O$. A small amount of calcium was present as admixed calcite. Neither water nor carbon dioxide is lost at 140° ; long heating at high temperature is necessary to expel these constituents completely. Two constitutional formulae are suggested: $ONa \cdot Al(OH) \cdot O \cdot CO \cdot OH$ and $Al(OH)_2 \cdot O \cdot CO \cdot ONa$, the first of which is considered the more probable. E. J. R.

Chemical Investigation of a Uranium Mineral from Borneo. G. P. TSCHERNIK (*Bull. Acad. Sci. St. Pétersbourg*, 1909, [vi], 3, 1203—1212).—This mineral occurs in well-formed, iron-black crystals, D^{25}_D 9.057, hardness 5—6, exhibiting marked radioactive properties. The analytical results of two different specimens are as follows:

SiO_2	UO_3	UO_2	PbO	ThO_2	Y_2O_3 , etc.	CaO	FeO
0.77	40.95	41.24	8.51	5.03	1.56	0.13	0.91
0.76	40.38	41.15	8.49	5.00	1.57	0.13	0.90

Bi_2O_3	MgO	CuO	H_2O	Total.	D^{25}_D
trace	trace	—	0.52	99.67	9.059
—	trace	trace	0.52	99.45	9.056

These numbers show that the mineral consists of brüggerite, the corresponding formula being:



Further analysis of the rare earth constituent shows that it contains yttria and ceria in the proportion $Y_2O_3 : Ce_2O_3 = 5 : 1$, the ceria fraction containing oxides of cerium, lanthanum, neodymium, and praseodymium in the proportions: $Ce_2O_3 : La_2O_3 : Nd_2O_3 : Pr_2O_3 = 8 : 5 : 1 : 2$. T. H. P.

Isomerism in the Group of Alumino- and Ferri-silicates. VLADIMIR I. VERNADSKY (*Bull. Acad. Sci. St. Pétersbourg*, 1909, [vi], 3, 1183—1202).—In addition to alumino-(or ferri-)silicates having the

structure of kaolinite (derivatives of clay), chloritoids (derivatives of $M_2Al_2SiO_6$), and chlorites [derivatives of $Al_2Si_{2+m}O_{4+2m-n}(OH)_n$ or $Al_2SiO_{3-n}(OH)_{2n}$], a group of aluminosilicates is possibly derived from orthosilicates, and having the general formula: $(M_2SiO_4)_pA$, where $A = MAl_2Si_2O_8$ (or $MFe_2Si_2O_8$) or MAl_2SiO_6 . To this group belong: (1) melilite, $(Ca_2SiO_4)_p qCaAl_2Si_2O_8$, where $p=3.5$ and $q=1.2$; (2) gehlenite, $Ca_2SiO_4CaAl_2SiO_6$, and (3) ilvaite, $H_2O-(Fe_2SiO_4)_p-CaFe_2Si_2O_8$, where $p=2$. In their properties these compounds differ from the compounds $MAl_2Si_2O_8$, and approximate to the minerals M_2SiO_4 . This series of silicates is analogous to the kaolinite series and to the granites isomeric with them.

Isomerism in the kaolinite series is of three kinds: (1) symmetry isomerism; (2) transposition isomerism, an example of which is shown by the granite, $CaAl_2Si_2O_8$ (nucleus), Ca_2SiO_4 , and the member of the melilite series, Ca_2SiO_4 (nucleus), $CaAl_2Si_2O_8$; (3) isomerism of rearrangement, as seen in lawsonite, $CaAl_2Si_2O_8 \cdot 2H_2O$, and Gibbsite, $H_2Al_2Si_2O_8 \cdot CaO \cdot H_2O$.

T. H. P.

Physiological Chemistry.

Acapnia and Shock. IV. Fatal Apnoea after Excessive Respiration. YANDELL HENDERSON (*Amer. J. Physiol.*, 1910, 25, 310—333. Compare Abstr., 1909, ii, 421).—One of the most marked symptoms of pain is hyperpnoea, and the drugs which relieve pain quiet breathing. The forced breathing leads to apnoea, owing to the carbon dioxide being swept out of the body; the apnoea in the end leads to the phenomena of shock; and, in fact, the symptoms of shock can be induced in normal men and animals by excessive ventilation of the lungs. This in animals can be carried so far as to be fatal. This is due to lack of oxygen, primarily produced by the inactivity of the respiratory centre, which is not excited owing to the absence of carbon dioxide. The administration of that gas during apnoea causes breathing to recommence. Failure of respiration after intense pain is produced in the same way.

W. D. H.

Union of Oxygen in Blood. WILHELM MANCHOT [and, in part, W. BRANDT] (*Annalen*, 1909, 370, 241—285).—An investigation on the relationship existing between the absorption of certain gases by blood and (1) the temperature, (2) the partial pressure of the gas, and (3) the concentration of the blood, carried out with the object of obtaining information on the absorption of oxygen by blood.

A complete analogy is found to exist between the metallic salts which combine with gases, and blood-pigment in their behaviour towards certain gases; thus, not only does blood-pigment combine with acetylene, carbon monoxide, ethylene, nitric oxide, and oxygen, but the dissociation is conditioned by the same factors as those which determine

the dissociation of the compounds of cuprous chloride with these gases (compare Manchot and Friend, *Abstr.*, 1908, ii, 375 Manchot and Brandt, this vol. i, 85).

The compounds of hæmoglobin with acetylene and ethylene are dissociated to the greatest extent, whilst the degree of dissociation of the oxygen compound is slightly greater than that of the compound with carbon monoxide or nitric oxide. Changes of temperature and pressure produce a greater effect on the ethylene compound than on the carbon monoxide compound; in the case of the former substance, the effect produced by altering the temperature is due rather to an alteration in the state of equilibrium than to the change in the concentration of the gas.

Blood which has been reduced by means of hydrogen, likewise natural blood, when diluted with water, serum, or isotonic solutions of sodium chloride or sucrose, combines with a greater proportion of oxygen, carbon monoxide, ethylene, or nitric oxide than undiluted blood. The same observation was made with the blood of horses, oxen, and pigs. The absorption reaches a maximum at a dilution of about eight to ten times, at which point each atomic proportion of iron is found to combine with practically two molecular proportions of the gas. The effect of further dilution, likewise the addition of alkali, is to decrease the absorption of gas, owing to the hydrolysis of the additive compound.

Since the gases, oxygen, carbon monoxide, nitric oxide, ethylene, and probably also acetylene, are absorbed in equimolecular proportions, it follows that the absorption of these gases by hæmoglobin is not brought about through the agency of individual valencies, but through the mutual attraction of the molecules as a whole with the formation of a molecular complex, as in the case of the union of cuprous chloride and carbon monoxide (*loc. cit.*).

Blood which has been acted on by hydrogen for some time after the complete reduction of the oxyhæmoglobin is found to absorb more oxygen than that which has not been thus treated; this is shown to be due to the presence of carbon dioxide, which is slowly removed by the hydrogen. Carbon dioxide in this respect behaves like hydrogen chloride with carbon monoxide and cuprous chloride (*loc. cit.*).

The latter part of the paper is devoted to a discussion of the absorption of oxygen by the blood in respiration, and the effect of carbon dioxide on the tension of the oxygen in blood. It is shown that the presence of uncombined hæmoglobin in the blood (natural blood contains roughly one molecular proportion of oxygen per atomic proportion of iron) tends to keep the velocity of absorption of oxygen under different pressures constant.

W. H. G.

Physiology of Water and Sodium Chloride. OTTO COHNHEIM, KREGLINGER and KREGLINGER (*Zeitsch. physiol. Chem.*, 1909, 63, 413—434).—An increase in the concentration of hæmoglobin in the blood was not observed with certainty at an elevation of 3000 to 4500 metres. In severe muscular work, a noteworthy dilution of the blood occurs. Profuse sweating leads to a decrease of chlorides in the body, which on the days following it, is succeeded by retention of chlorides.

The loss of chlorides may lead to a cessation of hydrochloric acid secretion in the stomach.

W. D. H.

Neutrality Equilibrium in Blood and Protoplasm. LAWRENCE J. HENDERSON (*J. Biol. Chem.*, 1909, 7, 29—36).—The power of proteins to preserve neutrality in solution, which is regarded as of great importance by Brailsford Robertson, is great, but under conditions obtaining in the organism, is not comparable with that of the inorganic constituents of blood and protoplasm. There is no proof that more than a small portion of the carbon dioxide liberated from the blood in the lungs comes from sodium hydrogen carbonate which has given up its sodium to proteins, according to a simple reaction which is reversed in the tissues. It is improbable that this is the chief reaction involved unless indirectly through the heterogeneous equilibrium between red corpuscles and plasma, including the movement of chlorine, ionised or otherwise, across the red corpuscle wall and the consequent liberation and fixation of carbon dioxide in the plasma.

W. D. H.

Influence of Stereochemical Configuration on Certain Physico-chemical Properties of Organic Colloids. GIUSEPPE BUGLIA and L. KARCZAG (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 474—481).—Investigation of the influences exerted by the various tartaric acids on the coagulation by heat of dialysed blood-serum (compare this vol., ii, 52) shows that the action of these acids is due mainly to the hydrogen ions when the acids are present in very small concentrations; when, however, the concentrations are relatively high, the actions are determined principally by the stereochemical configurations. So that, only when the concentrations are high, are differences observable between the actions of the different acids. The actions of the various tartaric acids on muscular proteins (gastrocnemius muscle of the frog) are, in general, analogous to those exerted on the neutral protein of dialysed blood-serum. Both in accelerating the coagulation of the blood-serum and rendering it non-coagulable, and also in determining the velocity of coagulation (contraction) of muscle by heat, the *l*-acid is more effective than the *d*-acid.

T. H. P.

Reversed Activity of Tissue Extract made at High Temperatures. BERTRAM J. COLLINGWOOD (*Proc. physiol. Soc.*, 1909, xiv—xv; *J. Physiol.*, 39).—At 115° a tissue extract loses its power to accelerate blood-coagulation. If the undissolved residue is extracted at this temperature, an anti-coagulant is formed.

W. D. H.

Glycolysis. I. The Susceptibility to Alkali of Dextrose. LEONOR MICHAELIS and PETER RONA (*Biochem. Zeitsch.*, 1910, 23, 364—369).—The difficulties of measuring glycolysis in the blood are mainly two; one, the difficulty of estimating sugar in a protein-rich fluid can be overcome by the authors' method; the other is the supposed loss of sugar due merely to the action on it of the alkali of the blood and tissues. It has been known for a long time that sodium hydroxide and sodium hydrogen carbonate cause dextrose to disap-

pear from solution; this is confirmed—the optical activity gets less and less, it being largely due to conversion into levulose or mannose. But the alkalinity of blood is not that which can be estimated by titration, but depends on the concentration of hydroxyl ions, and can be imitated by mixtures of primary and secondary sodium or potassium phosphates; such solutions cause no change in the optical activity or concentration of sugar in solution; the disappearance of sugar due to mere alkalinity of the blood is therefore a negligible factor.

W. D. H.

Physico-chemical Behaviour of Uric Acid and its Salts in the Blood. F. GUDZENT (*Zeitsch. physiol. Chem.*, 1909, 63, 455—477).—Uric acid can only exist in the blood as monosodium urate. In pure water this salt exists in two isomeric forms; the first (*a*-salt) is more soluble, but more unstable, than the other form (*b*-salt); the same is true for artificial and probably also for natural serum. Under certain conditions, for instance, in gout, the blood can be oversaturated with the urate, and this may lead to its deposition in the tissues, but no specific affinity between cartilage and uric acid exists.

W. D. H.

The Behaviour of the Anti-Substances of the Blood-Serum Towards Solvents and Other Reagents. K. KAWASHIMA (*Biochem. Zeitsch.*, 1909, 23, 186—192).—The anti-trypsin and anti-rennet action of the blood-serum was investigated. The serum was dried in a vacuum to a powder. The anti-properties were not appreciably altered by extraction with ether or ethyl alcohol. The anti-rennet action was, however, appreciably diminished by treatment with methyl alcohol, the anti-tryptic action being diminished by the same treatment only to a slight extent. The anti-rennet cannot be detected in the methyl alcohol. A small amount of the anti-trypsin dissolves in a mixture of equal parts of methyl alcohol and water. Acetone appears to render the anti-substances insoluble in water. Hydrogen peroxide and salicylaldehyde injure both anti-substances. Treatment with acids, alkalis, and ferments appears to exert no action on them.

S. B. S.

The Proportionality of Proteolytic and Rennetic Action of the Gastric Juice of Man and Dog in Normal and Pathological Cases. TH. J. MIGAY and W. W. SAWITSCH (*Zeitsch. physiol. Chem.*, 1909, 63, 405—412).—The experiments recorded show that the two properties of gastric juice referred to vary directly the one to the other both in normal and pathological conditions, and therefore support Pawloff's view that both are due to one and the same enzyme.

W. D. H.

Partial Transformation of Alimentary Fatty Matter into Mannitols by Peptic and Pancreatic Digestion in vitro. EMILE GAUTHRELET (*Compt. rend.*, 1909, 149, 1150—1151).—The author cites the results of experiments, from which he draws the conclusion that the artificial acid-peptic digestion of fatty materials, such as olive oil, butter, or tallow, converts these into *l*-mannitol,

whilst, when the digestion is pancreatic, in an alkaline medium the mannitol produced is dextrorotatory. The amount of mannitol produced depends largely on the state of division of the fat, and in the case of peptic digestion on the acidity of the solution.

W. O. W.

Action of Heat on Dry Pancreatic Extract. EUGÈNE CHOAY (*J. Pharm. Chim.*, 1910, [vii], 1, 10—16).—Various observers have recorded that the proteolytic activity of dry pancreatic extract is but little affected by exposure to a temperature of 100°. The author finds that exposure to a temperature of 80° or 100° during one or two hours scarcely affects the activity of the amylase, lipase, or trypsin present in pancreatic ferment, but that at 120° the activities of all three enzymes are rapidly paralysed. Of the three, the amylase seems to be affected least by heat. In solution, on the contrary, all three enzymes are rapidly affected by heat, thus mere desiccation of pancreatic ferment at 40° to 50° reduces the activity of the amylase by three-quarters and that of the lipase by one-half.

T. A. H.

Fat Cleavage by Pancreatic Juice. I. ÉMILE F. TERROINE (*Biochem. Zeitsch.*, 1910, 23, 404—427. Compare Abstr., 1909, ii, 497).—Addition of mono- or di-glycerides does not influence the cleavage of triglycerides by pancreatic lipase. The addition of oleic acid to an emulsion of olive oil hinders the process of saponification, but the addition of glycerol increases the rate of cleavage. This is specially the case for emulsions and solid fats; the action of glycerol is slight or absent in the case of fats soluble in water (mono-butylin, triacetin). Any viscous substance (gum, egg-albumin) has a similar favourable action. The optimum temperature for pancreatic lipase is 40°, but cleavage occurs even at 0°. Warming the lipase to 45° lessens its power, and to 65° destroys it. In presence of bile salts, it is more easily affected by rise of temperature. The enzyme acts in a neutral, but better in a faintly alkaline, medium (optimum *N*/150); it is lessened in acid or strongly alkaline media.

W. D. H.

Concentration of Anti-substances in the Body-fluids of Normal and Immune Animals. J. R. GREER and F. C. BECHT (*Amer. J. Physiol.*, 1910, 25, 292—309).—A research on similar lines to that carried out by Hughes and Carlson (Abstr., 1908, ii, 304), determining the amount of hæmolysins, agglutinins, precipitins, etc., in the various fluids of the body.

W. D. H.

The Purine Bases of the Bone-marrow. H. THAR (*Biochem. Zeitsch.*, 1909, 23, 43—44).—The following yields of purine bases were obtained from 1000 grams of bone-marrow: guanine 0·3125, adenine 0·1710, hypoxanthine 0·0724, xanthine 0·02875 gram.

S. B. S.

The Sugar Destructions in Animal Organisms which are Measurable by the Polarimeter. ALBERT J. J. VANDEVELDE (*Biochem. Zeitsch.*, 1909, 23, 324—328. Compare Abstr., 1908, ii, 714).—Extracts of liver and pancreas do not cause changes in the

rotation of lactose solution, such as the author has already shown occurs when this sugar is kept with milk. He has also followed the changes in the rotation of solutions of other sugar solutions when kept with animal fluids or extracts of organs. Dextrose solutions were not changed by extracts of organs. Urine caused a slight diminution of the rotation of lactose solution, and also of dextrose solution. The reducing powers in these cases were only slightly, if at all, altered.

S. B. S.

Lactic Acid in the Autolysed Dog's Liver. TADASU SAITAI (*J. Biol. Chem.*, 1909, 7, 17—20).—The lactic acid in autolysed dog's liver is largely sarco-lactic [*d*-lactic] acid, as in other organs. A small amount of fermentation-lactic acid is also observed even in the sterile condition.

W. D. H.

The Action of Mercury Salts on Autolysis. MARCO TRUFFI (*Biochem. Zeitsch.*, 1909, 23, 270—274).—It has been shown that mercury salts promote the autolytic process, and the author has determined the optimal quantities for various salts.

S. B. S.

Cholesterol Esters in the Human Epidermis and their Reactions. ERNST SALKOWSKI (*Biochem. Zeitsch.*, 1910, 23, 361—363).—The cholesterol ester of palmitic acid was separated from human epidermis, which was identified by its melting point, colour reactions, and elementary composition.

W. D. H.

The So-called Fat of Tissues and Organs. HUGH MACLEAN and OWEN T. WILLIAMS (*Bio-Chem. J.*, 1909, 4, 455—461).—The presence of "masked fat" in cell protoplasm is now recognised as a fact of physiological and pathological importance. The yield of "fat" differs with the extracting agent employed, according to its disintegrating action on protoplasm or the fat-products. The main material in the so-called fat is phosphatide, which may be free or combined. The organ chiefly investigated in the present research was the liver, but some details are also given of other tissues. The methods of extraction are also described.

W. D. H.

The Importance of Phosphatides for the Living Cell. II. WALDEMAR KOCH (*Zeitsch. physiol. Chem.*, 1909, 63, 432—442. Compare Abstr., 1903, i, 301).—In colloidal solutions of phosphatides, reactions are observed similar to those which occur in physiological material. Carbon dioxide and ammonia in small concentration affect lecithin emulsions, leading to alteration in its hydrogen-ion and hydroxyl-ion concentration. Phosphatides play their part in the morphological and chemical differentiation of cells, especially in regard to the formation of membranes.

W. D. H.

The Relationship of Diastatic Efficiency to Average Glycogen Content in Tissues and Organs. HUGH MACLEAN (*Bio-Chem. J.*, 1909, 4, 467—479).—Great variations occur in animals, even of the same species, in the diastatic efficiency of their tissues. Very often an

organ containing mere traces of glycogen (for instance, the lung) has a higher amylolytic power than the liver. Wohlgemuth has recently published similar results. There is, in fact, no definite correlation between glycogen content and diastatic efficiency in the case of adult tissues.

W. D. H.

Chemico-physical Investigations on the Crystalline Lens. FILIPPO BOTTAZZI and NOÉ SCALINCI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 423—430. Compare this vol., ii, 56).—The authors have examined the influence exerted by sodium chloride on the imbibition of the crystalline lens of the dog in solutions of acids and of sodium hydroxide (compare Abstr., 1909, ii, 502). The imbibition in 0.2*N*-sodium chloride solution is increased slightly by acids and very considerably by sodium hydroxide. In the latter case, the velocity and magnitude of the imbibition are proportional to the concentration of hydroxyl-ions, whilst with acids the amount of imbibition is directly proportional to the concentration of hydrogen-ions, hydrochloric and acetic acids favouring imbibition rather more than sulphuric acid of the same concentration.

From these and previous results, it is evident that alkalis are the most potent agents influencing the imbibition of the tissues, and that the extent of the physiological imbibition of every living cell and fibre corresponds with a certain relation between the concentration of the neutral salts and that of the salts which in aqueous solutions have alkaline reactions owing to hydrolytic dissociation. For a given concentration of hydroxyl-ions, the imbibition of the crystalline lens or of the tissues is greatest in absence of neutral salts. The absorption of the lens, muscles, etc., should be less in a solution of barium or calcium hydroxide than in one of sodium or potassium hydroxide of the same concentration.

T. H. P.

The Iodine Complex in Sponges. HENRY L. WHEELER and LAFAYETTE B. MENDEL (*J. Biol. Chem.*, 1909, 7, 1—10).—Drechsel's iodo-gorgonic acid from Gorgonian corals was shown to be 3:5-di-iodotyrosine by Wheeler and Jamieson (Abstr., 1905, i, 350). In sponges, also, it is now shown that the iodine is present in the same form. The common bath sponge served as the source of the material. The ease with which iodine enters into combination with the aromatic group suggests certain considerations respecting the function of iodine in proteins, some of which are commented on.

3:5-Di-iodotyrosine and the similar compound with bromine are precipitated by phosphotungstic acid, whilst tyrosine itself is not. It does not give the tyrosine reaction with Millon's reagent until after reduction.

W. D. H.

The Theory of Urea Formation. ALBERT A. EPSTEIN (*Biochem. Zeitsch.*, 1903, 23, 250—261).—According to Schmiedeberg's theory, urea is formed in the organism from ammonium carbonate; according to the theories of Salkowski and Hoppe-Seyler, urea is formed by the addition of ammonia to a substance in which a nitrogen atom is already bound to a carbon atom (for example, cyanates). If the

Schmiedeberg conception is correct, then there is no limit (except the toxicity) to the amount of ammonia which can be converted in the organism into urea. If the other theories are correct, then there is a limit, as the amount of cyanate or other groups available for synthesis depends on the protein degradation. In the latter case, if the amount of nitrogen in the ammonium salt ingested exceeds that derived from protein, the excess of ammonia should be excreted in this form and not as urea. Experiments carried out on rabbits by the author, in which the nitrogen of the ammonium salt (lactate) administered exceeded that of the normal nitrogen output on a fixed diet, lead to the conclusion that there is no limit to the amount of ammonium salt which can be converted into urea. The results, therefore, support Schmiedeberg's theory.

S. B. S.

The Origin of Lactose. CH. PORCHER (*Biochem. Zeitsch.*, 1910, 23, 370—401).—If the mammary glands are removed in cows and goats immediately after parturition, glycosuria of variable intensity sets in rapidly, and lasts about twenty-four hours. A similar result follows amputation of the breasts in lactating animals. This is associated with hyperglycaemia; lactose is not present. Phloridzin injection in suckling animals produces glycosuria as well as in lactating and male animals. In the operation cases just referred to, the sugar is dextrose, which, in the absence of the mammary glands, is not converted into lactose.

W. D. H.

Influence of Lactic Acid Ferments on Intestinal Putrefaction in a Healthy Individual. HELEN BALDWIN (*J. Biol. Chem.*, 1909, 7, 37—48).—A full account of a prolonged series of observations on a man which showed that sour milk exerted no specially favourable influence on the subject's condition. The excretion of ethereal sulphates and phenol in the urine, and of indole and scatole in the faeces, was usually increased when the fermented milk was taken.

W. D. H.

Experimental Glycosuria. V. The Distribution of Glycogenolytic Ferment in the Animal Body, especially of the Dog. JOHN J. R. MACLEOD and R. G. PEARCE (*Amer. J. Physiol.*, 1910, 25, 255—291. Compare Abstr., 1909, ii, 168).—Prolonged perfusion of the liver with isotonic salt solution does not lessen the power of the extracts of the organ to destroy glycogen; this is against the view that the action is due to lymph. The full amount of glycogenolysis is not obtained until the tissue cells are crushed in Buchner's press; the ferment responsible is therefore an endo-enzyme. This is termed glycogenase; it is most abundant in the pancreas, the liver and blood-serum (or plasma) come next, and then the kidneys, intestines, and muscles. The nutritive condition of the dogs used is not a factor in the activity, and the blood-serum from the pancreatic vein does not contain more of the enzyme than that from the carotid artery. The organs of pig, rabbit, and especially the lamb, are less active than those of the dog.

W. D. H.

The Urorosein Reaction. HENRY D. DAKIN (*J. Biol. Chem.*, 1909, 7, 57—58).—Herter has shown that indoleacetic acid is the chromogen of urorosein, and that the reaction is obtained when nitrites are also present in the urine. Ciusa and Terni (Abstr., 1908, i, 763) state that one of the derivatives of cinnamylideneacetophenone, the α -oxime, when given to animals causes the appearance of the urorosein reaction in their urine. This was repeated in the present experiments with negative results. It is suggested that the previous animals had a trace of indoleacetic acid in their urine, and that the administration of the oxime was followed by the occurrence of nitrites, for it is known that hydroxylamine is converted into nitrous acid in the organism.

W. D. H.

The Action of Saline Purgatives. ARTHUR F. HERTZ, F. COOK, and E. G. SCHLESINGER (*Guy's Hospital Reports*, 1909, 63, 297—307).—Two views are held in regard to the action of saline purgatives; one, the more prevalent supposes that the salt attracts water into the intestine and so produces fluid stools; the other supposes that the salt is absorbed and the effect is due to a specific irritation by the absorbed salt of the intestinal neuro-muscular and secretory mechanism, leading to increased peristalsis and increased secretion. The present paper is an argument in favour of the latter theory. It is pointed out that the purgation often occurs within half an hour, and that Röntgen-ray pictures of the intestine show that what is taken by the mouth does not reach the caecum until four hours later. This time is only very slightly shortened after a saline purge. Further, the watery contents which are increased consist of succus entericus, not simply of water; of the sulphate administered, the faeces show little, if any, increase, whilst into the urine the excess of sulphate passes very rapidly, showing that it has been absorbed.

W. D. H.

The Estimation of Ferments in the Faeces. HANS URY (*Biochem. Zeitsch.*, 1909, 23, 153—178).—The following data were determined: amount of faeces, total solids, weight of solids in aqueous extract, and the nitrogen in the total and the extract. The following ferments were quantitatively estimated in the aqueous extract: pepsin (by Volhard's method), amylolytic ferment (by Wohlgemuth's method), the pancreatic ferment (by Volhard's method), the lipase, the nuclease (by determination of the adenine yielded by thymus nucleoprotein), the maltase, and the invertin (by the usual polarimetric methods). The results were calculated in terms of 1 gram of dry substance or of 1 gram of nitrogen, except in the case of the pancreatic enzyme, which was calculated in terms of 0.01 gram of nitrogen. Pepsin was found to be always absent from faeces, and also lipase. Nuclease and maltase were present in the faeces after administration both of senna and magnesium sulphate, but absent in the normal faeces. After administration of the former drug, the ferments normally present in faeces (amylase, pancreatic ferment, and invertin) were in considerably increased quantities; this was not the case after magnesium sulphate administration. The author gives full details of his experimental methods.

S. B. S.

Chemistry of Cancer. II. Purine Bases, Creatine, and Creatinine. TADASU SAIKI (*J. Biol. Chem.*, 1909, 7, 23—26).—After removal of fat and lipoids from a number of cancerous tumours, the residue was hydrolysed with sulphuric acid, and purine bases determined by the Krüger-Schmid method. The following figures are given: uric acid, 0.024%; adenine as picrate, 0.032%; hypoxanthine as nitrate, 0.0034%; guanine and xanthine are only present in traces; this suggests the presence of guanase and oxydase, and the absence of adenase, as in other human tissues. Creatine and creatinine were determined by Folin's method; the creatinine present amounted to 0.016% of the fresh tissue; creatine was practically not present.

W. D. H.

The Influence of Certain Alcohols, Hydroxy- and Amino-acids of the Aliphatic Series on the Sugar and Nitrogen Excretion in Phloridzin Diabetes of the Dog. I. PAUL HÜCKENDORF (*Biochem. Zeitsch.*, 1909, 23, 281—303).—To starving dogs receiving phloridzin injections, various alcohols, amino-acids, and other substances were administered, and the alterations caused in the nitrogen and sugar excretions were noted. It was found that the administration of those alcohols which contain an uneven number of carbon atoms causes, almost always, an increased sugar excretion. In the case of propyl alcohol this increase is not regular. The alcohols with three and five carbon atoms caused a diminution of the nitrogen output. The alcohols with an even number of carbon atoms did not cause an increased sugar excretion; neither did *n*-valeric acid. In this case both the sugar and nitrogen excretion were somewhat diminished. Fermentation-lactic acid caused a slight increase of sugar excretion and diminution of nitrogen excretion; *d*-l-alanine caused a slight increase in the sugar, and also an increase in the nitrogen. Olive oil caused an increase in the nitrogen output.

S. B. S.

Phloridzin Diabetes. I. A. A. ERLANDSEN (*Biochem. Zeitsch.*, 1910, 23, 329—360).—Phloridzin glycosuria is not regarded as a primary hepatogenous or renal production of sugar, and so Minkowski's theory is held to be untenable. It originates owing to the passage of phloridzin through the kidney, calling forth there an abnormal elimination of sugar by that organ, which is probably a true secretion. The sugar in the blood is removed in this way, but as the amount of sugar in the carotid blood does not diminish, it is necessary to suppose that a secondary compensatory sugar production occurs in the liver, as Bang has proved to be the case. The maximal amount of sugar in the urine occurs simultaneously with the maximum of phloridzin excretion, and it ceases at the same time as, or shortly after, the excretion of phloridzin ceases.

W. D. H.

Gout. F. GUDZENT (*Biochem. Zeitsch.*, 1909, 23, 275—277).—Polemical. The author contends that the conclusions of Bechhold and Ziegler (*Abstr.*, 1909, ii, 916) are unjustified, as it is theoretically impossible for uric acid to exist as such in serum. It

must exist in the form of a sodium salt which will form supersaturated solutions, the degree of supersaturation of which will depend on rate of formation and other circumstances. He holds, also, that the conclusions of these authors are unjustified, because the analyses are incomplete, no account having been taken of the carbon dioxide tension of the solutions, and that it is impossible to entirely free the deposits analysed from serum and other substances. The author also states that other physico-chemical laws have not been taken into account in the investigations criticised.

S. B. S.

The Influence of Alcohol on the Quantity of Phosphatides in Animal Organs. NADINE SIEBER (*Biochem. Zeitsch.*, 1909, 23, 304—323).—The phosphatides were estimated in the organs of animals which had received alcohol, and in those of control animals which had received no alcohol, and had been kept under otherwise similar conditions. The organs of the former showed a smaller lecithin content than those of the latter, the diminution varying from 0.57% in the stomach wall to 11% in the brain, these numbers being the mean of several experiments.

S. B. S.

The Chemical Constitution and Physiological Action of Alcohols and Acids. II. JACQUES LOEB (*Biochem. Zeitsch.*, 1909, 23, 93—96. Compare Abstr., 1909, ii, 168).—The minimum quantities of alcohols necessary to convert negatively heliotropic copepoda into positively heliotropic organisms were determined. The higher the atomic weight of the alcohol, the greater was the activity. The same result was also obtained with daphnia. The narcotic effect was similar to the heliotropic effect. The heliotropic action of the acids is much stronger than that of alcohols. Hydrochloric, nitric, and sulphuric acids have about the same action as formic acid. The increased action of the fatty acids with higher molecular weights is not so marked as in the case of the alcohols.

S. B. S.

The Fate of Histidine in the Body of the Dog. KATHARINA KOWALCZKY (*Biochem. Zeitsch.*, 1909, 23, 1—4).—The ingestion of histidine hydrochloride caused an increase in the acidity in the urine (even when sodium carbonate was administered), and a large increase in the total nitrogen and ammonia output in the urine, the ratio of ammonia to total nitrogen being also increased. The results indicated degradation of the body proteins. Methyliminazole acted toxically when administered to a dog.

S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Action of Sodium Benzoate on the Multiplication and Production of Gas by Various Bacteria. CHRISTIAN A. HERTER (*J. Biol. Chem.*, 1909, 7, 59—67).—Food preparations containing 0.1% of sodium benzoate nearly always contain small numbers of bacteria,

chiefly of the spore-bearing kind. In dextrose bouillon, the same percentage only slightly inhibits *Bacillus coli* and other intestinal bacteria. Gas production may, however, be considerably hindered. When mixed faecal bacteria are introduced into dextrose bouillon containing 0.1 to 0.2% of sodium benzoate, the bacteria are unequally inhibited. In general, the organisms of the *Bacillus coli* type are more inhibited than cocci.

W. D. H.

Decomposition of Nitrates by Bacteria. S. A. SEWERIN (*Centr. Bakt. Par.*, 1909, ii, 25, 479—492. Compare Abstr., 1909, ii, 479).—Denitrification experiments with *Bacillus pyocyaneus* and *Vibrio denitrificans* showed that both microbes can frequently utilise dung, straw, and urine as a means of increasing denitrification in a marsh, whilst in a black soil these substances were not utilised, although the microbes grow readily in the soil without manure. In one experiment the addition of a very large amount of dung (8%) resulted in a reduction of the amount of nitrate by 17% when the soil was inoculated with *Bacillus pyocyaneus*, but no effect was produced with *Vibrio denitrificans*.

N. H. J. M.

Alcoholic Fermentation in the Presence of Sulphurous Acid. M. EMMANUEL POZZI-ESCOR (*Bull. Assoc. Chim. suc. Dist.*, 1909, 27, 561—562).—The author does not agree with the statement made by Martinand (Abstr., 1909, ii, 823) that yeasts do not ferment sugar solutions in the presence of sulphurous acid. Pure yeasts which the author employed in his experiments became acclimatised to the presence of this acid. It is also pointed out that the beer yeast used by Martinand does not under ordinary conditions readily ferment sucrose in acid solution.

W. P. S.

The Influence of Fermented Sugar Solutions on the Respiration of Wheat Seedlings. S. KOSTYTSCHOFF (*Biochem. Zeitsch.*, 1909, 23, 137—142).—Dextrose solutions were fermented by zymïn until they no longer exerted a reducing action on Fehling's solution; the alcohol was then distilled off. Seedlings soaked in such solutions showed an increased output of carbon dioxide, equivalent to 142% in twelve hours, as compared with seedlings which had been soaked in water. No increased alcohol production could, however, be detected, and the author assumes that the action is due to increased normal respiration, and not to alcoholic fermentation; the amount of oxygen used up, furthermore, does not increase in the same ratio as the carbon dioxide production.

S. B. S.

The Influence of Mineral Salts on the Respiration of Germinating Seeds. W. ZALESKI and A. REINHARD (*Biochem. Zeitsch.*, 1909, 23, 193—214).—The authors give the results of some preliminary investigations of the action of various salts on the seeds of *Lupinus angustifolius*, *Zea mays*, and *Pisum sativum*. The solutions investigated include Knop's solution and magnesium sulphate, potassium dihydrogen phosphate, potassium nitrate, magnesium sulphate, and other salt solutions, and also of solutions containing mixtures of salts. In each case the

output of carbon dioxide was measured and compared with the output of the same seeds grown in pure water. The results are expressed as the number of mg. of carbon dioxide expired per hour by one hundred seeds. The action of the salts was not the same on all the varieties of seed tested, and depends, perhaps, on the mineral content of them. Attention is called to the possible antagonistic action of various ions, such as has already been observed in other biological processes.

S. B. S.

The Part Played by Oxygen in the Formation of Protein in Plants. W. ZALESKI (*Biochem. Zeitsch.*, 1909, 23, 150—152).—The author has already shown that there is a considerably greater formation of proteins in the bulbs of *Allium cepa* which have been punctured as compared with intact bulbs (Abstr., 1901, ii, 619; 1902, ii, 348). He now extends this observation to pea seeds. A control was dried at 60—70°, and two other similar portions were kept, one in dry air, and the other in a dry oxygen-free atmosphere. The two latter portions contained more protein than the former, the portion which was kept in presence of oxygen containing the largest quantity of the three. There was no change in the amount of total nitrogen. The analyses were carried out by Stutzer's method. The author attributes the increased protein formation in oxygen to the increased energy supply to the seeds, and he assumes, therefore, that the action is only indirect.

S. B. S.

Selective Absorption of Ions by Roots. ENRICO PANTANELLI and M. SELLA (*Atti R. Accad. Lincei*, 1903, [v], 18, ii, 481—488).—By means of plantlets of dwarf *Cucurbita pepo*, the authors have investigated the selective action of the absorptive epithelium of the roots on the anions and cations of various salts. The results confirm the capacity of this membrane of functioning as a septum unequally permeable for different ions, the amounts of the latter absorbed for various salts being given, in mg.-ions, in the following table:

	KCl.	CaCl ₂ .	K ₂ SO ₄ .	CaSO ₄ .	KH ₂ PO ₄ .	CaHPO ₄ .
Cation	23.38	0	11.6	0	1.15	1.10
Anion	30.68	51.39	18.07	1.93	49.04	78.98

In the case of the four soluble salts, potassium chloride, calcium chloride, potassium sulphate, and potassium dihydrogen phosphate, the amounts of carbon dioxide emitted by the young roots were determined, not on comparing these amounts with those of the cations remaining in excess, no general rule is observable. With calcium sulphate and the phosphate CaHPO₄, however, it appears that, the more rapid the absorption of the anion compared with that of the cation, the more carbon dioxide is emitted by the roots. This phenomenon is based on, at least, the two following causes: (1) increase of the respiring surface and mass by the accelerated development of the roots produced by the alimentary and catalytic influences of the rapidly absorbed anions; (2) the direct influences of these anions on the respiratory activity.

T. H. P.

Nitrogenous and Mineral Composition of Ornamental Plants. ALEXANDRE HÉBERT and GEORGES TRUFFAUT (*Bull. Soc. chim.*, 1910, [iv], 7, 31—37).—With a view to the preparation of appropriate compound and complete manures for garden plants, the authors have determined the amounts of nitrogen and mineral constituents present, per kilogram of fresh plant, in a large number of species grown for horticultural purposes. These are tabulated in the original.

T. A. H.

Chlorophyll. VII. Comparative Investigation of the Chlorophyll of Different Plants. RICHARD WILLSTÄTTER, FERDINAND HOCHEDER, and ERNST HUG (*Annalen*, 1910, 371, 1—32. Compare Willstätter and Benz, Abstr., 1908, i, 199).—The existence of two distinct chlorophylls has been definitely established by Willstätter and Benz (*loc. cit.*). Crystalline chlorophyll is now shown to contain two methoxyl groups, whilst amorphous chlorophyll, from determinations with phaeophytin, contains one phytol residue and one methoxyl group for each atom of magnesium; phaeophorbins, derived from crystalline chlorophyll, is likewise a dimethyl ester.

The primary object of this investigation was to ascertain the extent of the distribution of these chlorophylls in the vegetable world, the method employed being as follows: the chlorophyll is extracted from the dry material by means of alcohol, and converted as completely as possible by oxalic acid into the magnesium-free decomposition product; the latter is then hydrolysed quantitatively, the weight of phytol obtained being a measure of the phaeophytin and, consequently, of the amorphous chlorophyll present in the plant.

Determinations made with grass, plantain, and stinging nettle, collected from various localities and at different times of the year, indicate that the nature of the chlorophyll is not influenced by these factors, a result not in accord, apparently, with the conclusion drawn by Borodin from his investigations (*Bot. Zeit.*, 1882, 40, 608).

The results of the analyses of the chlorophyll of seventy plants taken from thirty-six families are recorded. These show that phytol is distributed widely in nature; with the exception of one family (*Verbenaceae*), of which only one variety was examined, representatives of all the families investigated have been obtained in which phytol ester-chlorophyll preponderates. In six cases the proportion of phytol was small, namely, in *Stachys silvatica*, *Galopsis versicolor*, *Galopsis tetrahiti*, *Datura stramonium*, *Verbena officinalis*, and *Scrophularia nodosa*; crystalline chlorophyll was isolated from the first four, also from *Lamium maculatum*, which with *Atropa belladonna* and *Salix* occupies an intermediate position. The distribution of crystalline chlorophyll indicated by these results does not appear to be as great as was deduced by Borodin (*loc. cit.*) and Monteverde (*Atta Horti Petropolitani*, 1893, 13, 123).

The basic decomposition product obtained from the various preparations of phaeophytin from seventy plants is in the majority of cases principally a mixture of phytychlorin-*z* and phytyrhodin-*y*; the latter compound is the principal decomposition product of phaeophytin from *Pinus silvestris* and *Betonica officinalis*, whilst it is not present in the

decomposition product of phaeophytin from *Urtica dioica* and *Salix*. Analyses of the basic compounds just mentioned point to a larger proportion of carbon to nitrogen than that represented by the formulae given by Willstätter and Hocheder (Abstr., 1907, i, 780).

The proportion of chlorophyll in the leaves of various plants has been estimated colorimetrically by comparison of the alcoholic extract with a standard solution of crystalline chlorophyll; it is found to vary from 0.5% to slightly over 1% of the dry material, a value smaller than that given by Tschirch.

W. H. G.

Adenium Hongkel, the Ordeal Poison of the French Soudan. EM. PERROT and M. LEPRINCE (*Compt. rend.*, 1909, 149, 1393—1395).—An aqueous-alcoholic extract of the flowers of *Adenium Hongkel*, from Upper Senegal, showed intense toxic properties. By extraction with chloroform, a neutral, yellow, amorphous substance was obtained, agreeing approximately with the formula $C_{20}H_{31}O_6$. The substance has m. p. 84—85°, and is characterised by the reddish-violet coloration developed with sulphuric acid, and by its marked sternutative action. Physiological experiments suggest that it belongs to the group of cardiac poisons resembling stropanthine.

W. O. W.

Presence of a Glucoside, which is Decomposed by Emulsin, in the Leaves and Twigs of *Eremostachys laciniata*. JOSEPH KHOUMI (*J. Pharm. Chim.*, 1910, [vii], 1, 17—19).—The leaves and young shoots were extracted with alcohol, the solvent distilled off, and the residue dissolved in an aqueous solution of thymol. Of this solution, half was treated with invertase, when its optical rotation rose from $-14'$ to $36'$. It was then boiled to destroy the invertase, and, on cooling, emulsin was added. Under the influence of this ferment, the rotation changed to $+6'$, indicating the presence of a glucoside. This deduction was confirmed by the similar action of emulsin on an aqueous solution of that portion of the alcoholic extract soluble in a mixture of alcohol and ethyl acetate. Determinations of the amount of reducing sugar formed indicated that the glucoside present has not been described previously.

T. A. H.

A New Cupric Salt and its Application as a Fungicide for Diseases of the Vine and other Plants. PHILIPPE MALVEZIN (*Bull. Soc. chim.*, [iv], 5, 1096—1098).—See this vol., i, 91.

Oxidation Taking Place in Wines. PHILIPPE MALVEZIN (*Ann. Chim. anal.*, 1910, 15, 15—19).—In order to ascertain the action of various oxidising substances on wine, the author has made a number of experiments in which wine was treated with copper oxide, nitric acid, etc. Whilst simple aeration for a period of five minutes was without effect on the different constituents of the wine employed in the experiments, the addition of 125 grams of cupric oxide to 1 litre of wine caused, after a lapse of five and a-half hours, a decrease in the quantity of non-volatile acids and of glycerol present, whilst the amount of volatile acids showed a slight increase. In the case of another wine, which was treated with 0.2% of 40% nitric acid, and the action allowed

to continue for four days, the quantity of esters originally present was trebled; the glycerol, however, was diminished to the extent of about 30%. This action of the nitric acid was still more marked after twelve days' contact. The author agrees with the opinion of other observers that the presence of small quantities of iron and manganese has an effect on the formation of aldehydes and esters; he is also of opinion that it is not necessary that these metals should be derived from the soil by the grapes and pass into the wine as organic salts. It is possible that accidental contact with a metal will result in sufficient of the latter being dissolved to play an important part in the oxidation processes taking place subsequently in the wine. As cupric salts have such strong oxidising properties, it is advisable not to use copper vessels for containing wine, as even traces of the metal when dissolved may lead to alterations in the character of the wine. W. P. S.

Disappearance of Sulphur Dioxide. HUBERT (*Ann. Chim. anal.*, 1909, 14, 453—454).—The author attributes the rapid disappearance of sulphur dioxide from wines, not to oxidation, but to the formation of a stable combination with substances of an aldehydic nature. This may be shown experimentally by adding to sulphited wines a little urotropine (hexamethylenetetramine); the amount of total sulphur dioxide is at once reduced. L. DE K.

Difference of Races and Individual Beets with Regard to their Composition. KARL ANDRLIK, V. BARTOŠ, and J. URBAN (*Zeitsch. Zuckerind. Böhm.*, 1910, 34, 221—237).—Different races of sugar-beet, grown under the same conditions, show differences in composition, especially in the pure ash. The ash of roots with high percentage of sugar contains more calcium, magnesium, and phosphoric acid, and less sodium, than roots with low percentage of sugar; and they contain less alkalis to 100 parts of sugar.

Individual roots of different races, grown under the same conditions, may show essential variations in composition.

The amount of mineral constituents taken up per 100 parts of sugar varies both in individual roots of different races and of the same race. Roots with high percentages of sugar now take up less inorganic bases than was found to be the case by Walkhoff in 1874.

N. H. J. M.

Analytical Chemistry.

Manipulation of Small Precipitates. Qualitative and Quantitative Micro-chemical Analysis. FRIEDRICH EMICH and JULIUS DONAU (*Monatsh.*, 1909, 30, 745—757).—Micro-filters of paper are cut about 6—8 mm. in diameter, and placed on the thickened end of a capillary tube, which is cut square and polished. The tube acts as a funnel, and is placed in a suitable apparatus so that suction can be

applied. The application of a little vaselin to the rim of the filter, and its depression in the centre over the capillary by means of a glass rod, enables large drops to be filtered without danger of any loss owing to the liquid flowing off the paper. The precipitate is collected on the filter, washed, and placed in a sheet of platinum foil, which can be wrapped round it, and so prevent loss during drying, ignition, and weighing. A Nernst micro-balance was used for the weighings. A number of simple qualitative and quantitative estimations have been performed accurately and quickly in the manner described. E. F. A.

Apparatus for Filtering at a Constant Temperature. ALFRED EISENSTEIN and FRIEDRICH ZIFFER (*Chem. Zeit.*, 1909, 33, 1330).—The apparatus consists essentially of a filtering tube surrounded by a constant-temperature jacket, the constant temperature being maintained either by a freezing mixture or by circulation of a liquid of known temperature. The filtering tube is made of three lengths of glass-tubing of different widths, the two upper sections being contained in the constant-temperature jacket. A piece of platinum or copper wire gauze is placed at the lower joint, and on this can be placed the filter paper. The upper joint is ground to fit the elongation of the bulb of a thermometer, so that the top tube can be cut off from the middle one. If a substance is to be extracted at a constant temperature, it is placed in the middle section of the filtering tube, above the wire gauze; the upper joint is then closed by the thermometer, and the solvent poured into the top tube. When everything has attained a constant temperature, the thermometer is raised and the solvent allowed to percolate through the contents of the middle section.

The estimation of paraffin in paraffin shale, by Holde's method, is described to illustrate the working of the apparatus. T. S. P.

The Influence of Neutral Salts on Indicators. LEONOR MICHAELIS and PETER RONA (*Biochem. Zeitsch.*, 1909, 23, 61—67).—The influence of various neutral salts on the shade of the indicator colour was investigated, the hydrogen-ion concentrations being chosen for each particular indicator in which the latter is most sensitive, according to the determinations of Friedenthal. In some cases the addition of salt alters the nuance, so as to indicate increased acidity, in others, increased alkalinity. In the case of Congo-red, the authors think the change is due to the action of the salt in precipitating the dye; in other cases, they assume the change to be due to a different dissociation constant of the indicator in the new medium. The correction due to the presence of salts is negligible when the concentration reaches 1/8 normal (a concentration met with physiologically), except in the case of methyl-violet, Congo-red, and neutral-red. When necessary, a correction can be made in the Friedenthal method by adding salt to the control solution. The disturbing influence of proteins is much greater than that due to salts. S. B. S.

A New Sensitive Indicator. Dimethyl-Brown. M. EMMANUEL Pozzi-Escot (*Bull. Assoc. Chim. Sucr. Dist.*, 1909, 27, 560—461).—The indicator is prepared by treating anthranilic acid in hydrochloric

acid solution with an excess of nitrous acid at the ordinary temperature; the diazo-substance obtained is combined with *p*-dimethylaniline, and the product is boiled with a large excess of hydrochloric acid and *p*-dimethylaniline hydrochloride. The solution is filtered while hot, and the filtrate is saturated with sodium chloride. The precipitate formed adheres to the sides of the vessel containing the mixture, and is washed rapidly with cold water. On dissolving the precipitate in alcohol, a solution is obtained which shows a brown coloration in neutral or acid aqueous solutions; alkalis change the colour to yellow.

W. P. S.

Systematic Detection of the More Important Acids. THADDEUS MILOBENDSKI (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1301—1306).—The method devised by Abegg and Herz (*Abstr.*, 1900, ii, 436) for the separation and identification of acids, besides omitting several important radicles, possesses several disadvantages. Thus, the barium (group III) and calcium salts (group II) are very similar in their solubilities, and if excess of the reagent is used, the calcium precipitate always contains radicles belonging to group III; further, the detection of thiocyanates in the form $(\text{FeCNS})_3$ masks the presence of iodides.

The author has modified the system so as to avoid these disadvantages. After giving a number of preliminary tests, he proceeds to the systematic scheme, the various groups being as follows:

(1) Strontium group, including phosphite, phosphate, arsenite, arsenate, sulphite, carbonate, tartrate, oxalate, fluoride, sulphate, and part of the borate. (2) Lead group, used if an iodide is present and containing iodide and sulphide; thiocyanate detected in the filtrate. (3) Zinc group, precipitated from the filtrate from group (1) and containing cyanide, ferro- and ferri-cyanide, and sulphide. (4) Silver group, comprising thiosulphate, iodide, bromide, chloride, and thiocyanate; chlorate and acetate detected in the filtrate. Details are given for the examination of the various group precipitates.

T. H. P.

The Detection of Hydrofluoric Acid in Presence of Fluorides. WALTER CRONHEIM (*Biochem. Zeitsch.*, 1909, 23, 143—146).—As hydrofluoric acid is used as an antiseptic in food-stuffs, from which it is afterwards precipitated in the form of an insoluble salt, it is of importance to know whether traces of the acid remain in products which have been treated in this manner. As hydrofluoric acid is insoluble in alcohol and ether, whereas the salts are soluble, the two solvents are added to the sample under investigation. The fluorides are slowly precipitated from the supernatant liquid; the free acid remaining in solution is precipitated by calcium or barium hydroxide. In these two precipitates, fluorine can be detected by Hefelmann's (glass-etching) method, which can detect 1 part in 800,000.

S. B. S.

Action of Iodine on Sodium Dithionate or Trithionate in Solution. JOSEPH A. MULLER (*Bull. Soc. chim.*, 1909, [iv], 5, 1119—1121).—The object of this work was to ascertain whether

sodium thiosulphate could be estimated in presence of sodium dithionate or trithionate by titration with standard iodine solution. It was found that both the dithionate and the trithionate decolorise iodine solution when their solutions are warmed, but that in cold solutions, either neutral or acidified with acetic acid, the action is so slow that sodium thiosulphate can be safely titrated with iodine in their presence.

T. A. H.

Volumetric Estimation of Selenious Acid in Alkaline Solution by Permanganate. LUIGI MARINO (*Zeitsch. anorg. Chem.*, 1909, 65, 32—37).—None of the usual methods of titrating selenious acid are trustworthy under all conditions. Titration with permanganate in acid solution gives an uncertain end-point, but good results are obtained in alkaline solution according to the equation: $2\text{KMnO}_4 + 3\text{SeO}_2 = \text{K}_2\text{O} + 2\text{MnO}_2 + 3\text{SeO}_3$. The $N/5$ -permanganate solution is prepared by dissolving 6 grams of potassium permanganate in 800 c.c. water, and adding 40 grams of potassium carbonate and 0.4 gram of potassium hydroxide; $N/5$ -oxalic acid is used to standardise the solution. The selenious acid solution is made just alkaline with sodium hydroxide, titrated with permanganate, heating, and stirring well until the supernatant liquid is violet. It is then acidified with sulphuric acid and titrated with oxalic acid until all the manganese dioxide has dissolved. After cooling to 80—90°, the excess is titrated with permanganate.

Low results are obtained in the presence of chlorides, owing to the volatility of selenium chloride. Nitrates should be removed by evaporating with zinc sulphate and dilute sulphuric acid. The method is applicable to insoluble selenites.

C. H. D.

Estimation of Total Nitrogen in Urine. HUGUET (*Ann. Chim. anal.*, 1909, 14, 453).—Five c.c. of pure sulphuric acid are introduced into a 500 c.c. flask, which is then placed in an inclined position on a wire gauze and heated until sulphuric fumes appear. A mixture of 10 c.c. of urine and 25 c.c. of sodium persulphate solution (20 grams in 100 c.c.) is now added drop by drop, and the whole is then heated again until quite colourless. When cold, 10 c.c. of water and 2 drops of phenolphthalein are added, and the liquid is neutralised carefully with pure aqueous sodium hydroxide; $D 1.26$. After diluting to 100 c.c., an aliquot part is taken for the gasometric estimation of the nitrogen by the hypobromite method.

L. DE K.

Source of Error in Estimating Ammonia. ÉTIENNE BARRAL (*Bull. Soc. chim.*, 1910, [iv], 7, 8—9).—It was found that in using Schloesing's method for the estimation of nitrogen as ammonia, new black-tin worm condensers absorbed considerable quantities of ammonia, and accurate results were only obtained after the condensers had been used some time. Granulated tin absorbed only traces of ammonia, so that probably the loss was due to the presence of grease or tin oxides in the new condensers.

T. A. H.

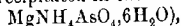
Estimation of Nitrogen in Nitrates by Reduction with the System Aluminium-Mercury. M. EMMANUEL POZZI-ESCOFFIER (*Compt. rend.*, 1909, 149, 1380—1381).—Not more than 0.5 gram of the

nitrate is treated in a Schloesing flask with 4 to 5 grams of aluminium turnings and a few drops of mercuric chloride solution; a little water is then added, and, after some minutes, when the action has ceased, a little alkali. After distilling off the ammonia, some sodium hypophosphite is added to decompose mercurammonium compounds.

The process has given excellent results with soils and manures.

W. O. W.

Detection of Arsenic Acid in Presence of Arsenious Acid by means of Magnesia Mixture. OSCAR LUTZ and R. SVISSE (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1488—1491).—Magnesia mixture being recommended by many authors as a means of detecting arsenic acid and its salts in presence of arsenious acid (only the ion of the arsenic acid being precipitated in the form of the salt,



the authors have tested the reaction in presence of various proportions of ammonia and ammonium salts. The results show that, in presence of a sufficiently large amount of arsenious acid, the separation of arsenic acid by means of ordinary magnesia mixture is impossible. Further, aqueous or ammoniacal solutions of arsenious acid are less sensitive to the action of magnesia mixture than solutions of sodium and potassium arsenite. Qualitative separation may be attained under certain conditions of dilution, that is, for concentrations of the arsenious ion less than $M/200$ if ordinary magnesia mixture is employed, or less than $M/50$ if a large proportion of ammonium salts is present; but at such dilution, the lower limit of sensitiveness for arsenic acid may be passed. But, as the proportions of the two anions are usually unknown, and as the operation of dilution is too complicated for qualitative purposes, this method of separating the arsenic from the arsenious ion is not practicable.

T. H. P.

Detection of Boric Acid in Butter and Milk. E. GARTER (*Ann. Chim. anal.*, 1910, 15, 14—15).—A portion of the butter is melted with a small quantity of hot water, the aqueous layer is separated, filtered, and the filtrate is treated with a few drops of barium hydroxide solution. After the addition of a little alcohol, the mixture is subjected to centrifugal action, the clear solution is decanted, and the precipitate is treated with about 1 c.c. of hot concentrated oxalic acid solution. The barium oxalate, which dissolves in the excess of oxalic acid, is reprecipitated by the addition of alcohol and separated. The clear alcoholic solution is then evaporated after the addition of a few drops of an alcoholic solution of turmeric. As the evaporation proceeds, the edges of the liquid show a red coloration should boric acid be present, and eventually a red residue is obtained. The coloration is given by as little as 0.0001 gram of boric acid. In the case of milk, the test is applied to the ash.

W. P. S.

Ultimate Analysis of Coals Containing [Hydrated] Clays. A. LISSNER (*Chem. Zeit.*, 1910, 34, 37—38).—If coals containing clay are submitted to the usual ultimate analysis, a large proportion of the

water collected is due to combined water contained in the clay, which a previous drying at 120° has failed to remove. The author, therefore, recommends the removal of the hydrated clay before proceeding to combustion.

The weighed portion of the sample is heated on the water-bath with a mixture of 2 vols. of fuming hydrofluoric acid and 1 vol. of hydrochloric acid; D 1.18. A twice or thrice repeated evaporation suffices to decompose the silicate. The residue is then treated with hot water, and collected on a dried and weighed filter. After drying at 100° , the filter and contents are submitted to the usual organic combustion. Allowance is made for the carbon and hydrogen yielded by the filter-paper, which may be taken as consisting of pure cellulose.

When dealing with samples chiefly consisting of clay, the process is as follows: The carbon is estimated in about 1 gram of the sample as usual. A similar quantity of the sample, which need not be weighed accurately, is then treated with acid as described, and collected on a filter. After drying for two hours at 100° , the carbonaceous matter is detached from the filter, and also submitted to analysis. In this way the proportion of hydrogen to the carbon is found, and the amount of carbon in the sample being accurately known, the hydrogen is found by a simple calculation.

L. DE K.

Estimation of Carbon Monoxide in Air. E. GOUTAL (*Ann. Chim. anal.*, 1910, 15, 1—7).—A portable apparatus is described for the estimation of carbon dioxide, the process employed depending on the oxidation of the monoxide to dioxide by means of iodic anhydride according to the equation: $5\text{CO} + \text{I}_2\text{O}_5 = \text{I}_2 + 5\text{CO}_2$. The iodic anhydride is contained in a tube, and is heated for some hours in a current of oxygen at a temperature of 200° before being used. During the estimation, the tube and its contents are heated to a temperature of 70° by means of a water-jacket, and the air under examination is drawn through the tube after having passed successively through wash-bottles containing acidified copper sulphate solution, potassium hydroxide solution, and concentrated sulphuric acid respectively. A filter, consisting of a tube filled with cotton-wool, may be placed before the wash-bottles. The volume of air drawn through the tube is ascertained by measuring the volume of water leaving the aspirator, and the rate of flow is regulated at about 1 litre per hour. The iodine liberated by the action of the carbon monoxide on the iodic anhydride is collected in a vessel containing either chloroform and water or potassium iodide solution; this vessel is placed between the exit end of the tube and the aspirator. The iodine collected is estimated by comparison with standard iodine solutions or by titration with standard thiosulphate solution. The process may also be employed for the estimation of the occluded carbon monoxide in steel; for this purpose, the steel is dissolved in potassium cupric chloride solution, and the gases evolved are passed, together with a current of pure air, through the tube containing the iodic anhydride.

W. P. S.

[**Estimation of** Carbon Monoxide in Steels. E. GOUTAL (*Compt. rend.*, 1909, 149, 1129—1131).—Compare this vol., ii, 129.

Titration by means of Borax in Presence of Glycerol. N. TANANAEFF and D. TSUKERMAN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1469—1481).—Borax in presence of glycerol may be employed to titrate, not only pure alkali hydroxide, but also, on boiling, alkali hydroxide containing carbonate (compare Rupp, *Abstr.*, 1907, ii, 194). The titration may be effected by adding alkali hydroxide to a solution containing borax and glycerol, and also by adding a solution of borax to one containing alkali hydroxide and glycerol. Titration with borax in presence of glycerol affords an excellent method of estimating alkali hydroxide in presence of carbonate.

T. H. P.

Estimation of Zinc in the Presence of Iron. JAMES M. TAYLOR (*J. Soc. Chem. Ind.*, 1909, 28, 1294—1295).—The process is based on the fact that a dilute neutral solution of zinc is precipitated by hydrogen sulphide with liberation of the acid, whilst ferrous salts are not affected.

Five to ten c.c. of the solution containing 0.1—0.3 gram of zinc are put into a flask, 20 c.c. of saturated solution of ammonium chloride are added, and any free acid is carefully neutralised with $N/2$ -sodium hydrogen carbonate, with a drop of methyl-orange as indicator; 100 c.c. of saturated solution of hydrogen sulphide are now added, and the solution is titrated with $N/2$ -sodium hydrogen carbonate, which should be added at first at the rate of 2 or 3 drops per second, and afterwards, when the precipitate turns grayish, more slowly. The end-point is reached when the colour changes to a decided chocolate (formation of iron sulphide). One c.c. of $N/2$ -sodium hydrogen carbonate = 0.016 gram of zinc. In this process it is necessary that the iron should be in the ferrous state, and no other metals precipitable by hydrogen sulphide should be present.

L. DE K.

New Volumetric Method for the Estimation of Copper. JEAN A. SANCHEZ (*Bull. Soc. chim.*, 1910, [iv], 7, 9—17).—The process depends on the precipitation of the copper as cupric ferrocyanide, and the solution of this, in a solution of potassium cyanide, previously standardised against a copper solution of known strength. The change in colour from the reddish-brown of copper ferrocyanide to the faint greenish-yellow of potassium cuprocyanide is used as indicating the end-point.

The precautions to be observed are as follows: the solution titrated should contain the equivalent of not more than 0.1 gram of metallic copper, and must be exactly neutralised; it must be free from iron, lead, zinc, nickel, cobalt, or manganese, and should contain no ammonia or ammonium salts. The results are not influenced by the presence of tin, antimony, or arsenic, or by most organic acids, provided the latter are exactly neutralised. Exact details for using the method are given in the original, which also contains two tables of results obtained by its use.

T. A. H.

Volumetric Estimation of Lead with Alkaline Permanganate. JULIUS F. SACHER (*Chem. Zeit.*, 1909, 33, 1321—1323).—A criticism of Bollenbach's method (*Abstr.*, 1908, ii, 68) for the

volumetric estimation of lead by means of alkaline permanganate. In Bollenbach's earlier experiments he found that one molecule of permanganate oxidised 3 atoms of lead, but later experiments (Abstr., 1909, ii, 1054) gave the number 3.34. The author shows that the latter figure is probably due to the sodium hydroxide used containing carbonate. He also finds that with increasing concentration of sodium hydroxide, the amount of lead nitrate necessary for the reduction of a given quantity of permanganate decreases, the temperature of experiment being 75—80°. Only when a series of estimations is carried out under exactly the same conditions do the results agree, and even then, the average error is 0.4% Pb, and is probably caused by varying temperature in different experiments; the lower the temperature the more lead nitrate is necessary for complete reduction of the permanganate. The action of varying concentrations of sodium hydroxide is probably due to its solvent effect on the lead sesquioxide, resulting in the re-formation of sodium plumbite. The method is quite untrustworthy for estimating the lead in materials containing lead sulphate.

T. S. P.

Substitution of Bromine and of Iodine for Chlorine in the Separation of Cerium from the other Cerium Earths. PHILIP E. BROWNING and EDWIN J. ROBERTS (*Amer. J. Sci.*, 1910, [iv], 29, 45—46).—The authors state that Mosander's process (passing chlorine through a solution of an alkali hydroxide containing in suspension the hydroxides of the cerium group) may be improved by substituting bromine for chlorine. At the first treatment some 50% of the admixed earths are removed, and, after two more treatments, a deposit of pure ceric hydroxide is obtained. It is important to remove the excess of bromine each time by heating on a water-bath.

Iodine also oxidises the cerium and causes the other earths to pass into solution, but the reaction is too incomplete to be of any analytical value.

L. DE K.

Estimation of Chromium in Chrome Iron Ore. JOSEPH A. MULLER (*Bull. Soc. chim.*, 1909, [iv], 5, 1133—1136).—Three methods were investigated, using pure chromium sesquioxide as the analytical material.

In the first process, the oxide was fused with a mixture of sodium hydroxide and potassium nitrate, and the chromate formed, after cooling, was dissolved in water, the solution acidified with sulphuric acid, and boiled to decompose nitrites. It was then reduced by sodium sulphite, and the chromium precipitated with just sufficient ammonia. This precipitate was heated with sodium hydroxide and hydrogen peroxide solution, the excess of the latter being finally removed by prolonged boiling. The solution was then diluted to a known volume, and an aliquot portion titrated with potassium iodide and sodium thiosulphate (Abstr., 1909, ii, 96). This gave a result equivalent to 99.6% of the theoretical.

In the second process the sesquioxide was fused with a mixture of sodium peroxide and potassium hydroxide. The aqueous extract from this was filtered to remove a trace of silver derived from the crucible

used, boiled during forty minutes, diluted to a known volume, and the chromium in an aliquot portion determined as lead chromate, or by titration with sodium thiosulphate (*loc. cit.*). By this latter method, the process gave a result equal to 99.2% of the theoretical.

The Blodget-Britton process, depending on heating the sesquioxide with potassium chlorate and soda-lime, did not give good results owing to the difficulty of extracting all the chromate from the insoluble residue.

Chromite, even after grinding in a porphyry mortar, requires fusing four or five times in succession before it can be completely dissolved by either of the first two processes. For each part of the mineral, four of sodium hydroxide and eight of potassium nitrate, or five of sodium peroxide and eight of potassium hydroxide, are needed for each fusion. The aqueous extract of the fused product should be treated with a few drops of alcohol to remove any manganese present.

Both processes give equally good results with chromite, and the second is much more rapid, although it entails greater wear on the silver crucibles used.

T. A. H.

Estimation of Tungsten in Tungsten-Steel. LUDWIG WOLTER (*Chem. Zeit.*, 1910, 34, 2).—0.2—0.5 Gram of the sample, which need not be finely powdered, is fused in a covered platinum crucible with 0.5—1.5 grams of potassium pyrosulphate, and, when sulphuric fumes escape, the flame is removed for half a minute and another 4.5—13.5 grams of pyrosulphate are added in two portions. The mass is now heated gradually to redness and kept so for fifteen minutes. The lid is removed, and, when cold, the fusion is treated with 60—75 c.c. of water and boiled with 20 c.c. of hydrochloric acid. The tungstic acid is collected, washed with 10% ammonium nitrate solution, then dissolved in hot dilute ammonia, and evaporated in a weighed platinum crucible. On igniting the residue, pure tungstic acid is left.

Traces of tungstic acid retained in the acid liquid may be recovered by evaporating to dryness, heating the residue for one to two hours at 120—130°, and then boiling with dilute hydrochloric acid, which leaves the tungstic acid undissolved. If the presence of silica is suspected, this may be expelled by evaporating a few times with a few drops of hydrofluoric acid.

L. DE K.

Separation of Vanadium, Molybdenum, Chromium, and Nickel in Special Steels. M. EMMANUEL POZZI-ESCOL (*Compt. rend.*, 1909, 149, 1131—1132; *Ann. Chim. anal.*, 1910, 15, 7—10).—The hydrochloric acid or nitric acid solution of the steel is heated to boiling and treated with a large excess of strongly alkaline sodium hypobromite. After boiling for some minutes, the insoluble iron and nickel hydroxides (also those of manganese and cobalt, if these metals are present) are filtered from the solution containing the chromate, molybdate, and vanadate of sodium. The precipitate is dissolved in dilute hydrochloric acid, and the solution again treated with alkaline hypobromite in order to get into solution all traces of chromium, molybdenum, and vanadium.

The iron and nickel are then readily separated, as also the chromium, molybdenum, and vanadium by the usual methods.

T. S. P.

Estimation of Antimony by Gutzzeit's Method. CHARLES R. SANGER and EMIL RAYMOND RIEGEL (*Zeitsch. anorg. Chem.*, 1909, 65, 16—24. Compare Sanger and Black, *Abstr.*, 1908, ii, 64).—A special form of reduction apparatus is used, in which the gas evolved passes through a small chamber containing a disk of filter-paper saturated with lead acetate solution, which removes hydrogen sulphide and supplies the moisture required for the production of a regular antimony deposit. The mercuric chloride paper is cut into strips 6—7 cm. long and 4 mm. wide, and stored in the dark over calcium chloride. The reduction with zinc and hydrochloric acid is continued for thirty minutes, and the mercuric chloride paper, which is not coloured unless the antimony exceeds 0.07 mg., is developed by means of *N/1* ammonia for five minutes. The length of the dark band thus produced is compared with a standard series of strips prepared with known quantities of antimony. Organic matter, except tartaric acid, must be absent, and the conditions of experiment must be exactly observed. The practical limit of sensitiveness of the method is about 0.001 mg. Sb_2O_3 , which is a smaller quantity than can be recognised with certainty by Marsh's test.

C. H. D.

Analysis of Columbites and Tantalites. GABRIEL CHESNEAU (*Compt. rend.*, 1909, 149, 1132—1135).—The mineral is dissolved by heating with a mixture of potassium hydrogen sulphate and sulphuric acid. The solid mass which is obtained on cooling is dissolved in water, the solution filtered, and the filtrate, after neutralisation with ammonium hydroxide, heated to boiling in order to precipitate the columbium and tantalum as pentoxides. The washed precipitate is digested for twenty-four hours with a tepid solution of ammonium sulphide, and then washed with cold 5% hydrochloric acid. While moist, it is treated with potassium fluoride and hydrogen fluoride in order to obtain the tantalofluoride and columboxyfluoride of potassium, which are then separated by the less solubility of the former in water.

The filtrates from the pentoxides of columbium and tantalum contain iron, manganese, etc., which are estimated in the ordinary way. The pentoxides also contain the silica and titanium dioxide present in the mineral; the silica is estimated by treatment of a known weight of the pentoxides with hydrofluoric acid.

The titanium is estimated colorimetrically by means of hydrogen peroxide, the colour not being affected by the presence of columbium and tantalum; the pentoxides containing the titanium dioxide are dissolved by treatment with a mixture of potassium hydrogen sulphate and sulphuric acid.

T. S. P.

Process for the Rapid Estimation of Alcohol. D. SIDERSKY (*Bull. Assoc. Chim. Sucr. Dist.*, 1909, 27, 562—563).—The method proposed depends on the complete miscibility of ether with concen-

trated alcohol. Twenty c.c. of the alcoholic liquid, wine for instance, under examination are placed in a stoppered tube, 10 c.c. of ether, D 0.724, are added, and 98% alcohol is run in from a burette in successive small quantities, the mixture being shaken after each addition. At first the ether separates out as a layer, but when sufficient alcohol has been added, the ether mixes completely with the alcoholic solution. The quantity of alcohol added is then noted, and is a measure of the amount of alcohol present originally in the sample. The burette employed is graduated so as to give directly the quantity of alcohol in the sample; it is a patented piece of apparatus, and it is quite possible that an ordinary burette graduated empirically may be used in its place.

W. P. S.

New Method for Detecting Traces of Alcohols. E. DE STAECKLIN (*Compt. rend.*, 1910, 150, 43—45. Compare Abstr., 1910, i, 196, 198).—A description of a method for the detection of alcohols, based on their conversion into aldehydes by a peroxydase system. A few drops of the liquid to be examined are rendered very slightly acid with acetic acid. The mixture is then treated with two drops of a solution made by adding a ferric salt to a hot freshly prepared solution of quinhidrone and containing 0.1% of iron. A few drops of a 5% solution of hydrogen peroxide are added, and the mixture shaken. Schiff's reagent is employed to recognise the aldehydes formed; if present, ferric tannate is substituted for the iron-quinhidrone, and the operations repeated; under these conditions, glycerol gives no result. Deniges' reaction (Abstr., 1909, ii, 272—273) is recommended in conjunction with the foregoing as a sensitive test for glycerol.

W. O. W.

Detection of Resorcinol by means of the Cyano-cupric Reaction. VOLCY-BOUCHER and J. GIRARD (*Ann. Chim. anal.*, 1910, 15, 13—14).—When a neutral or slightly acid resorcinol solution is mixed successively with copper sulphate solution and a small excess of potassium cyanide solution, a bright green fluorescence is observed. The reaction takes place in the cold, and the reagents must be added in the order mentioned. The reaction is given by a solution containing as little as 0.1 gram of resorcinol per litre.

W. P. S.

The Methods of Lecithin Estimation. JOSEPH NERKING (*Biochem. Zeitsch.*, 1909, 23, 262—269).—Brain was submitted to fractional extraction with acetone, light petroleum, benzene, absolute alcohol, 85% alcohol, and ether, and the phosphorus determined in the extracts. These experiments led to no method for quantitatively separating the lecithin. Attempts were then made to quantitatively precipitate the lecithin from various solutions in organic solvents by means of pure acetone, and acetone to which various acids or salts had been added. It was found that egg-lecithin could be quantitatively precipitated from ethereal solution by acetone if, to the latter, a few drops of (cold) saturated alcoholic solution of magnesium chloride had been added. From other solvents and by the other methods tried (acetone solutions of tartaric acid, etc.), the precipitation was incomplete.

S. B. S.

Volumetric Estimation of Sugars by K. Lehmann's Process. ERWIN RUPF and F. LEHMANN (*Arch. Pharm.*, 1909, 247, 516—526).—Fehling's solution and a solution of the sugar are boiled for a suitable time, cooled, and poured into a mixture of potassium iodide, dilute sulphuric acid, and water, the liberated iodine being then titrated with $N/10$ -sodium thiosulphate. Dextrose, levulose, invert sugar, maltose, lactose, starch, dextrin, invert sugar in wine, maltose in beer, and lactose in milk have been estimated by this process or by slight modifications of it. C. S.

Separation of Sucrose and Lactose by the Bulgarian Ferment. L. MARGAILLAN (*Compt. rend.*, 1910, 150, 45—47).—Bertrand has shown (*Abstr.*, 1909, i, 623) that the lactic organism from curdled Bulgarian milk is capable of converting lactose almost quantitatively into lactic acid, but is without action on sucrose. It is possible, therefore, to estimate the latter in mixtures containing lactose or dextrose by treatment with the Bulgarian ferment, followed by inversion and determination of the reducing power.

W. O. W.

The Method of Estimating Sugar in Urine. IVAR BANG and JÖSTA BOHMANNSSON (*Zeitsch. physiol. Chem.*, 1909, 63, 443—454).—A defence of Bang's method (*Abstr.*, 1907, ii, 136) against certain criticisms which have been made in reference to it.

W. D. H.

Cambridge's Reaction. LÉON GRIMBERT and R. BERNIER (*J. Pharm. Chim.*, 1909, [vi], 30, 529—536).—The authors state that Cambridge's reaction (*Lancet*, 1904) is obtained with all urines, and that the active principle formed by the hydrolysis with hydrochloric acid is glycuronic acid, which yields an osazone, m. p. 130—132°.

L. DE K.

Detection of Reducing Substances in Urine. C. J. REICHARD (*Pharm. Zeit.*, 1909, 54, 1007).—The author applies the gold-iodine reaction (*Abstr.*, 1909, ii, 262) for the detection of reducing substances in urine, and also for their identification. The presence of reducing matters may be shown by placing in a test-tube 8 c.c. of water, 0.5 c.c. of neutral 1% sodium aurichloride solution, and 0.1 c.c. 1% potassium iodide solution, 1 c.c. of normal urine is next added, and the whole left for twelve to fifteen hours. The mixture first turns violet, and then gradually deposits a blue precipitate, which is examined microscopically. The precipitate may be purified by shaking the liquid, first with ether, and then, after evaporation of the ether, with chloroform. If sodium thiosulphate is cautiously added, the chloroform turns a violet-blue.

For the identification of urine, one drop of the gold solution, one drop of the potassium iodide solution, and two drops of the supposed urine are placed on an object glass and dried for twelve hours over sulphuric acid. The slide is then examined microscopically, and will

show the characteristic crystalline, blue iodine compounds of urea, uric acid, and creatinine.

L. DE K.

The Quantitative Estimation of Amino-acids in Urine by means of Formaldehyde Titration. WALTHER FREY and ALFRED GIGON (*Biochem. Zeitsch.*, 1909, 22, 309—315).—The ammonia was first driven off from the urine, and estimated by Spiro's modification of the Folin method (by means of a current of air after addition of barium hydroxide solution and alcohol, the ammonia being received in standard acid). The residue was diluted to a definite volume, in an aliquot part of which the amount of acid necessary for neutralisation with $N/5$ -hydrochloric acid, using rosolic acid as indicator, was determined. Another aliquot portion was then neutralised with the experimentally-determined necessary amount of acid, and in this solution the amino-acids were estimated by titration with alkali after addition by neutral formaldehyde in the usual manner, phenolphthalein being employed as indicator.

S. B. S.

The Quantitative Estimation of Amino-acids, Polypeptides, and Hippuric Acid in Urine by means of Formaldehyde Titration. VALDEMAR HENRIQUES and SÖREN P. L. SÖRENSEN (*Zeitsch. physiol. Chem.*, 1909, 63, 27—40).—The hippuric acid can be estimated by extracting the urine with ethyl acetate, hydrolysing the residue after evaporation of the solvent with hydrochloric acid, and then, after driving off the excess of mineral acid, estimating the glycine formed during the hydrolysis by the usual formaldehyde titration method. The polypeptides can be estimated by hydrolysing the urine, after separation of the hippuric acid, by hydrochloric acid, and then, after getting rid of excess of the mineral acid, estimating the amino-acids in the usual way. The difference between the number thus obtained and the amino-acid number obtained before hydrolysis gives a measure of the quantity of polypeptides present in the urine. The authors also give details as to the use of indicators in the ordinary formaldehyde titration method.

S. B. S.

The Formaldehyde Titration of Amino-acids in Urine. TANZO YOSHIDA (*Biochem. Zeitsch.*, 1909, 23, 233—244).—The author shows that the formaldehyde titration method of Sørensen and Henriques for estimating amino-acid nitrogen gives generally satisfactory results. Only in the presence of large quantities of ammonium salts are the numbers obtained appreciably too low. He gives the results of a number of analyses of both normal and pathological urines.

S. B. S.

Detection of Biliary Acids, Lævulose, Glycuronic Acid, and Pentoses in Urine. ADOLF JOLLES (*Chem. Zeit.*, 1909, 33, 1238—1239).—Polemical. A reply to the criticisms of Wittels and Welwart (Abstr., 1909, ii, 1057), in which the author recapitulates his methods and upholds their accuracy.

L. DE K.

Detection of Biliary Acids [and Acetone]. RODOLFO FRITSCH (*Zeitsch. anal. Chem.*, 1910, 49, 94—96).—Jolles's process, boiling with rhamnose and strong hydrochloric acid, is recommended instead of the Pettenkofer sugar-sulphuric acid test. The rose coloration, changing to a green fluorescence, is characteristic for biliary acids. These acids may be separated from amines by precipitating with a 3% solution of casein and sulphuric acid, and then extracting from the precipitate with absolute alcohol. If to dilute solutions of acetone are added a few drops of a 5% solution of rhamnose, and then an equal volume of strong hydrochloric acid, the liquid when heated turns a magenta colour, which is very permanent. 0.01 Gram of acetone in 1 c.c. of liquid may thus be detected. L. DE K.

Thiocyanates in Tobacco Smoke. JULIUS TÓTH (*Chem. Zeit.*, 1909, 33, 1301).—The presence of thiocyanates in tobacco smoke may be proved by passing the fumes of a dozen cigars through two wash-bottles, each containing 100 c.c. of water, and adding to the mixed filtered liquids, copper sulphate and sulphurous acid. The precipitate is then collected and treated with aqueous sodium hydroxide; after acidifying with hydrochloric acid, the liquid will give the red colour with ferric chloride, disappearing on addition of mercuric chloride, or the aqueous solution may be mixed with zinc sulphate, which causes an abundant precipitate. The filtrate is then acidified with nitric acid, and, after adding copper sulphate solution, heated to 80°; the precipitate obtained is washed and treated with ferric chloride, when it will give a red coloration.

The amount of thiocyanate present may be estimated by passing the fumes of a dozen cigars through washbottles, each containing 100 c.c. of milk of lime. The united filtrates are evaporated and mixed with copper sulphate and excess of sulphurous acid. The copper thiocyanate is then converted by ignition into oxide and weighed as such, or Alt and Volhard's process—conversion of the thiocyanate into sulphate (*Zeitsch. anal. Chem.*, 1896, 35, 315)—may be used.

L. DE K.

New Test for Strychnine. PAUL MALAQUIN (*J. Pharm. Chim.*, 1909, [vi], 30, 546—549).—One c.c. of a solution of a strychnine salt (about 1:1000) and 1 c.c. of pure hydrochloric acid are placed in a test-tube, and 1 gram of pure and clean zinc cuttings is added. After four minutes, the liquid is rapidly heated to boiling and then cooled. The solution is carefully poured down the sides of a test-tube containing 2 c.c. of pure sulphuric acid. Either at once or within a few minutes, a rose-coloured ring will be noticed; after a time the colour gradually spreads through the acid. The contents may also be shaken so as to accelerate the reaction. The colour is not altered on boiling, and in this way there is no danger of mistaking veratrine, which also turns red, for strychnine.

The colour is destroyed by potassium thiocyanate, but not by sulphur dioxide. Ammonia discharges the colour, but acids again restore it. None of the other alkaloids or glucosides (of which a list is given) show the reaction. Hydrogenation of strychnine may also

be effected in alkaline solution by means of sodium amalgam, but this operation is less convenient. Strychnine may be extracted by agitating its salts with ether in the presence of an alkali. The ether is then shaken with dilute hydrochloric acid, and, after warming to expel the ether, the liquid is treated with zinc as just directed. L. DE K.

Estimation of the Xanthine Bases in Cocoa and Chocolate. A. PROCHNOW (*Arch. Pharm.*, 1909, 247, 698—711).—The author has tested the processes of Hilger and Eminger, of Dekker and Welmans, of Beckurts and Fromme, and Katz's modification of the last, for the estimation of theobromine and caffeine in cocoa and chocolate. Katz's process is the best, if carried out as follows: Six grams of powdered cocoa or 12 grams of powdered chocolate, 197 grams of water, and 3 grams of dilute sulphuric acid are boiled under a reflux condenser for thirty minutes in a tared litre flask. After the addition of 400 grams of water and 8 grams of magnesium oxide, the boiling is continued for one hour. Water, 30 to 50 grams, is added to compensate for that evaporated, the mixture is well shaken, and its weight, excluding that of the cocoa or chocolate, is determined. A portion of the liquid, five-sixths of the weight (corresponding with 5 grams of cocoa or 10 grams of chocolate), is filtered, and evaporated almost to dryness. The residue is dissolved in water, the solution is made up to about 25 c.c., treated with 25 drops of liquefied phenol, and extracted with chloroform in a Katz percolator for six hours. The chloroform in the extraction flask is evaporated, the phenol is carefully removed from the warm flask by the aid of the bellows, and the flask is dried until the weight is constant. C. S.

Estimation of Purine Nitrogen in Urine. STANLEY R. BENEDICT and TADASU SAIKI (*J. Biol. Chem.*, 1909, 7, 27).—The Krüger-Schmid method of estimating purine nitrogen gives low and irregular results. Satisfactory results can, however, be obtained by first rendering the urine acid by adding 20 c.c. of glacial acetic acid to each 300 c.c. of urine. W. D. H.

New Reactions of Thiocarbamide. T. SATO (*Biochem. Zeitsch.*, 1909, 23, 44—45).—The following reactions are described: coloration with acetic acid and potassium ferrocyanide (green changing to blue), with hydrochloric acid and potassium ferrocyanide, and with the ferrocyanide alone. The rate of development and disappearance of the colour varies in the three methods of carrying out the reaction. With sodium carbonate and ferrocyanide, a pink to violet colour gradually develops. This reaction is sensitive in dilutions of 1 in 10,000 to 1 in 20,000 of the urea derivative. S. B. S.

A New and Sensitive Reaction of Scatole. TAKAOKI SAKAKI (*Biochem. Zeitsch.*, 1910, 23, 402—403).—If 3 c.c. of scatole solution are mixed with 3 drops of methyl alcohol, and an equal volume of concentrated sulphuric acid added, a violet ring is formed at the place of contact; on shaking the fluids together, the whole mixture becomes violet-red. Dilutions up to one in five millions give the test. It is not given by tryptophan, indole, or by 2-methylindole. W. D. H.

Estimation of "Saccharin" [α -Benzoic sulphinide] in Various Foods. GUISEPPE TESTONI (*Zeitsch. Nahr. Genussm.*, 1909, 18, 577—587).—The estimation of "saccharin" in foods and beverages is rendered somewhat complex by the presence of other substances which are extracted together with the "saccharin" by the usual solvents. The following methods of separating the "saccharin" from such substances are shown, from the results of actual experiments, to be trustworthy. Should the ether-extract contain benzoic acid in addition to the "saccharin," the extract may be heated at 110—115° until the whole of the benzoic acid has sublimed; the "saccharin" remains unchanged, and may then be weighed. The benzoic acid may also be removed by steam distillation. Another alternative is to precipitate the "saccharin" from an alcoholic solution of the ether-residue by means of silver nitrate; the silver compound formed has the formula $\text{AgC}_6\text{H}_4\text{SO}_3\text{N}$, and may be dried at 100° before weighing. In the case of wines, beer, aerated beverages, syrups, etc., the ether-extract will contain tartaric acid, citric acid, tannin, and other substances; these may be destroyed by oxidation with permanganate, and the "saccharin" then extracted from the evaporated solution. In the presence of salicylic acid, the ether residue may be weighed, and the salicylic acid then estimated in the usual way, the amount of "saccharin" present being found by difference, or the salicylic acid may be precipitated by means of bromine and the "saccharin" then extracted with ether, after removing the bromine compound by filtration. In cases where the ether-residue contains fatty substances, essential oils, etc., the oxidation process may be applied for the removal of any tartaric or citric acids present, and the sulphur then estimated in the purified residue of "saccharin"; or the "saccharin" may be hydrolysed by boiling with hydrochloric acid, and the ammonia formed then estimated. Pure "saccharin" yields 7.65% of ammonia.

The author finds that a mixture of equal parts of ether and light petroleum is the best solvent to use for the extraction of "saccharin" from its solution. W. P. S.

Estimation of Tannin [in Catechu]. G. C. A. VAN DORP and J. RODENBURG (*Chem. Weekblad*, 1909, 6, 993—998).—The authors state that the only process which gives fairly satisfactory results in the assay of catechu is the process known as the Hunt-Loeventhal (titration with permanganate in presence of indigotinsulphonic acid before and after treatment with solution of gelatin).

The separation of non-tannin matters from tannins by means of hide powder, gives quite erroneous results. In one instance a sample of catechu gave 61.7% of tannin, but when another specimen of hide powder was used, only 34.3% was obtained. L. DE K.

The Detection of Blood-pigment by its Absorption of the Violet End of the Spectrum. OTTO SCHUMM (*Zeitsch. physiol. Chem.*, 1909, 63, 478—483).—Details are given of the methods for studying the details of the absorption bands in the violet and ultraviolet region of the spectrum which hæmoglobin and its

derivatives exhibit, and which Gamgee, among others, called attention to. By suitable means an aqueous solution of blood examined in a thickness of 1 centimetre exhibits this absorption in dilutions of 1 in 4000 to 5000. W. D. H.

The Estimation of Pepsin by the Clarification of a Turbid Solution of Egg-white. S. HATA (*Biochem. Zeitsch.*, 1909, 23, 179—185).—The egg-white solution is prepared by diluting egg-white in a mortar to five times the original bulk with water, filtering, heating at 60° for twenty minutes, and filtering again through muslin. A turbid solution is thereby obtained, which can be kept unchanged for several months. For the purposes of the test, this solution is again diluted with water to ten times its bulk. Into a series of test-tubes varying quantities of the pepsin-containing liquid are introduced, and diluted to 1 c.c. 0.5 c.c. of *N*/10-hydrochloric acid and 2 c.c. of the diluted suspension are then introduced, and the time of clarification is noted. The procedure is then similar to that employed in the ricin and odestin methods. The time of clarification is approximately inversely proportional to the dilution. S. B. S.

Employment of the Guaiacol Method for the Quantitative Estimation of Peroxydase. JULIUS BRUNN (*Ber. Dent. bot. Ges.*, 1909, 27, 505—507).—In employing Ostwald's method (*Abstr.*, 1907, ii, 976), quite fresh solutions of the resin must be used, as distinct amounts of peroxydase are formed in a few hours. A special defect is the use of drops of a strong resin solution instead of c.c. of a more dilute solution. The rate of the reaction should be determined, and not the final amount of colour.

The following method is recommended: A scale of colours of different intensity is prepared by diluting a blue water colour emulsion (Prussian blue with a little cadmium yellow and white). The back of the test-tube stand, which is placed in a window, is covered with tissue paper to avoid reflexions. The extracts in test-tubes are treated with hydrogen peroxide, and a little concentrated (golden-yellow) solution of guaiaconic acid (1 c.c. to 10—15 c.c. extract, to which 0.2 c.c. H_2O_2 /20 had been added) poured on. The tubes to be compared are shaken simultaneously to mix the contents, and the increase in intensity of the colour observed at definite intervals and compared with the tube scale; the more rapid the coloration, the greater the amount of peroxydase (compare Euler and Bolin, *Abstr.*, 1909, i, 863). N. H. J. M.

A Test for Mushrooms. M. LÖWY (*Chem. Zeit.*, 1909, 33, 1251).—An aqueous infusion of *Agaricus campestris* gives with sulphuric acid, D 1.86, a deep violet coloration. The reaction is best carried out as a ring test. The colour disappears on warming. The author has not as yet succeeded in isolating the active principle. Infusions of other fungi do not give the reaction. L. DE K.

General and Physical Chemistry.

Pulfrich's Ratio between Volume Contraction and Refractive Power of Liquid Mixtures. EDMOND VAN AUBEL (*Compt. rend.*, 1910, 150, 210—213).—Pulfrich has established the relationship: $(R - R_0)/R = q(D - D_0)/D = qc$ for binary mixtures, where R denotes the refraction and D the density of the mixture, R_0 and D_0 the refraction and density respectively which the mixture would have shown had there been no volume change on mixing, whilst q is a positive constant. The author shows, by calculation from results obtained by Wintgen (*Thesis*, Bonn, 1908), that in the case of a mixture of aqueous solutions of tartaric acid and ammonium heptamolybdate, q is negative. W. O. W.

Molecular Refraction of Isomerisable Unsaturated Acids and their Salts. ARTHUR HANTZSCH and KURT MEISENBURG (*Ber.*, 1910, 43, 95—105. Compare Brühl, *Abstr.*, 1904, i, 969; 1905, i, 70).—The molecular refraction of nitroethane and nitropentane in ethyl alcohol and in potassium ethoxide solutions shows that the relationship between the two nitro-compounds in ethyl-alcoholic solution is perfectly normal. The difference is 13.83, and the value for 3CH_2 is 13.80.

The results also show that the effect of the solvent on the refraction is not marked. Similarly, *p*-chloro- or *p*-bromo-phenol has practically the same molecular refraction in alcohol and in sodium ethoxide solutions.

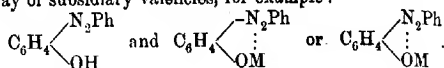
A comparison of *p*-nitrophenol and *p*-nitroanisole proves that the phenol in isobutyl butyrate, acetone, and methyl-alcoholic solutions is a true phenol, the difference between the two compounds being practically the value due to CH_3 . On the other hand, the *p*-nitrophenol in methyl alcohol and potassium methoxide solution shows a difference of 9.67 units; this undoubtedly indicates that the salts are derived from the *aci*-phenol. The following numbers give the increments in the mol. refractions of the three nitrophenols when transformed into their salts:

	<i>p</i> .	<i>o</i> .	<i>m</i> .
Mol. ref. D	9.68	4.26	1.80
Mol. ref. α	7.87	3.63	1.71

The molecular refraction and also the colour of solutions of nitrophenol indicate that it is partly converted into the *aci*-derivative.

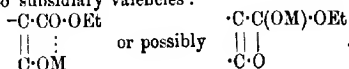
With *o*- and *p*-benzaldehydes the following increments due to salt formation were obtained: ortho 3.20, para 4.88, results which point to the conclusion that the salts cannot be simple phenolic salts. It is pointed out that the relationships between colour and molecular refraction are not so simple as stated by Kauffmann (*Die Ansochrome*, 65).

The refraction of the azo-group, calculated from the value for azobenzene, is 13.95, whereas in ethyl diazoacetate it has the value 8.41. The values for *p*-hydroxyazobenzene, its ethyl ether, and its acetyl and propionyl derivatives agree with the normal hydroxylic structure for the free hydroxy-compound. The value for the hydroxy-compound is somewhat increased when ethyl alcohol is used as solvent, probably owing to the formation of an additive compound. The values for the salts show an increment of some 12 units. This is attributed not to structural molecular rearrangement, but, as due to the play of subsidiary valencies, for example:



Similarly, the large increments noticed by Brühl in the salt formation of ethyl acetoacetate are not necessarily due to a structural alteration (enolisation), but may be due to the calling into play of subsidiary valencies.

It is pointed out that the molecular refraction of the salts is greater than that of the true enolic alkyl and acyl derivatives, and therefore this high exaltation can only be due to a further constitutive change due to subsidiary valencies:



J. J. S.

Theory of Dispersion in Gaseous Substances. LADISLAS NATANSON (*Bull. Acad. Sci. Cracow*, 1909, 907—915).—Recent measurements of the dispersive power of nitrogen, oxygen, hydrogen, carbon monoxide, carbon dioxide, methane, hydrogen sulphide, sulphur dioxide, helium, and argon have been made use of to test a deduction made by the author from Lorentz's electronic theory of absorption. The calculations based on these data indicate with some degree of probability that the product $\alpha \cdot \Delta$, in which α is the number of dispersion electrons contained in a molecule of a gas, and Δ the constant in the equation: $(n^2 + 2)/(n^2 - 1) = \Delta(1/\lambda_0^2 - 1/\lambda^2)$, has the same value for all gases. The average value of $\alpha \cdot \Delta$ is $16.3 \times 10^{-18} \text{ cm}^2$, and although in certain cases the experimental data of different observers differ widely, the author considers that sufficient evidence has been obtained to justify the conclusion that there is a close connexion between dispersion and valency.

H. M. D.

The Long-waved Portion of the Spectrum of Titanium. PAUL FIEBIG (*Zeitsch. wiss. Photochem.*, 1910, 8, 73—101).—The author has made a detailed photographic investigation of the line and band spectra of titanium between λ 4200 and λ 7360. For the production of the spectrum, metallic titanium was introduced into a cavity made in the positive electrode of a carbon arc, and the requisite large dispersion was obtained by a Rowland grating having a radius of curvature of 6.6 metres and 26,000 lines to the inch. The measured wave-lengths together with the estimated intensities are

recorded in tabular form, and the results compared with those previously obtained by Thalén, Hasselberg, and Rowland.

H. M. D.

Investigation of the Sodium Spectra. HANS ZICKENDRAHT (*Ann. Physik*, 1910, [iv], 31, 233—274).—The author has examined in detail the emission spectra obtained from the arc discharge between electrodes of different materials in an atmosphere of sodium vapour, and from the glow discharge under different conditions with and without an interposed spark gap. The consequent variations in the emission spectrum are described in detail.

In the second part of the paper, a summary is given of spectral observations relating to sodium, and these are discussed in reference to the author's measurements.

H. M. D.

Spectra of the Erbium Compounds and Stark's Valency Hypothesis. KARL A. HOFMANN and HEINZ KIRMREUTHER (*Zeitsch. physikal. Chem.*, 1910, 71, 312—324).—Stark (compare Abstr., 1908, ii, 574) has suggested a theory of valency based on the assumption that at the surface of a chemical atom there are positively charged spheres and minute negative electrons. When the atom enters into chemical combination, the lines of force from certain of the electrons become attached to the positive spheres on the other atom (saturated valency electrons); other electrons are not affected, their lines of force remaining attached to the positive spheres of their own atom (unsaturated valency electrons), while a third kind of electrons are affected in such a way that their lines of force are partly separated from the positive spheres of their own atoms (loosened electrons). According to Stark, the band spectra of the unsaturated valency electrons have their lower limit, at least in some cases, in the unattainable ultraviolet, $\lambda = 0.06\mu$, the band spectra of the saturated valency electrons lie in the ultra-red above $\lambda = 0.5\mu$. Hence in the visible region only the absorption due to the loosened valency electrons is of importance. The work of the authors on the spectra of erbium compounds supports Stark's theory.

The spectra of a number of solid anhydrous erbium salts were first measured at different temperatures by concentrating on them the light from the positive carbon of an arc lamp by means of a quartz lens, and examining the reflected light by means of a double prism instrument.

The spectra of erbium sulphide and chloride are very similar, and the change from chloride to oxide, and from oxide to sulphate, only brings about displacements of $1-3\lambda$ in the absorption bands, so that the electrons concerned in the absorption are not the saturated ones affecting the combination between erbium and the other elements or groups. Similarly, the effect of temperature in displacing the absorption bands is very slight, whereas the chemical linkings produced by saturated electrons are very greatly affected by change of temperature. On the other hand, the addition of water to the salts produces a great alteration in the spectra, and it is suggested that this is due to hydrate formation with participation of the "loosened" electrons.

The saturated valencies may, therefore, correspond with Werner's "Hauptvalenzen" (principal valencies), the valencies due to the loosened electrons with Werner's "Nebenvalenzen" (subsidiary valencies).

From an examination of the groups of absorption bands of the binary anhydrous erbium compounds, the conclusion is drawn that the effects are produced by three "loosened" electrons, which, with the three "saturated" valencies, make a total of six, corresponding with Werner's co-ordination number. G. S.

Flame Spectrum of Iron at a High Temperature. GUSTAVE A. HEMSALECH and CHARLES DE WATTEVILLE (*Compt. rend.*, 1910, 150, 329—332. Compare Abstr., 1908, ii, 445, 547).—When sparks are passed through an oxygen-acetylene flame between iron electrodes, the spectrum shows fewer lines than the simple flame spectrum. The lines are more intense than those obtained with the oxy-hydrogen flame. Some of the lines are identical with those seen in the blue cone of the Bunsen burner. A comparison is made in tabular form showing the relative intensities of lines in the two flames. Lockyer's enhanced line, λ 3935.92, has been observed, but apart from this the lines are those characteristic of low temperatures, and are only visible in traces in the spectrum of the electric furnace. W. O. W.

Measurements in the Long-waved Spectrum. HEINRICH RUBENS and H. HOLLNAGEL (*Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 26—52).—The authors have examined the ultra-red rays of very great wave-length which are obtained as the result of selective reflexion at the surfaces of polished plates of crystals of sodium chloride, potassium chloride, bromide and iodide. The wave-length measurements were effected by means of a quartz interferometer, the ready absorptibility of the long-wave rays necessitating, however, special arrangements in connexion with the details of the apparatus.

The residual rays, which were examined by a micro-radiometer after reflexion at four surfaces of the substance under investigation, form two bands of different intensity in the case of sodium chloride, potassium chloride, and potassium bromide. Although not definitely indicated by the data for potassium iodide, it seems probable that this grouping is also characteristic of potassium iodide. The mean wave-lengths of the bands are recorded for the first three salts, and it is found that these wave-lengths increase with the molecular weight of the salt.

As a result of the experiments with potassium bromide and iodide, the known spectrum has been extended by half an octave in the remote ultra-red region. The known part of the ultra-red region is thus approximately seven times as long as that of the visible spectrum. H. M. D.

Absorption Spectra of Various Salts in Solution and the Effect of Temperature on Such Spectra. HARRY C. JONES and W. W. STRONG (*Amer. Chem. J.*, 1910, 43, 97—135).—A continuation of the work described previously (this vol., ii, 87). A review is given of recent spectroscopic investigations. Attempts have been made to obtain the Zeeman effect for the absorption bands of uranyl chloride

and neodymium salt solutions, but without success. It is hoped, however, that the Zeeman effect may be obtained with solutions of erbium salts.

In studying the effect of change of temperature on the absorption spectra of salts, spectrograms have been made of the spectra of aqueous solutions at various concentrations of cobalt chloride (alone and in presence of aluminium chloride and of calcium chloride), cobalt thiocyanate, nickel acetate and sulphate, copper bromide, copper chloride (alone and in presence of aluminium chloride and of calcium chloride), uranyl chloride, nitrate, acetate and sulphate, uranous chloride and sulphate, praseodymium chloride, neodymium nitrate and bromide, neodymium chloride (alone and in presence of calcium chloride), and erbium chloride.

The results are discussed in the light of the electron hypothesis.

It has been found that the effect of a rise of temperature of an aqueous salt solution is to increase the general absorption and also to broaden and intensify the bands, and that, as a rule, the increase of the general absorption is much greater in concentrated than in dilute solutions.

The presence of calcium and aluminium chlorides causes the chromium chloride bands to widen very unsymmetrically on the long wave-length edge as the temperature rises.

The uranyl chloride bands are shifted towards the red with rise of temperature. The uranyl acetate and sulphate bands are also slightly shifted, but those of the nitrate are not affected in this way.

In the case of the neodymium and erbium salts, the bands do not appear to be shifted as the temperature increases. In presence of calcium chloride, however, the neodymium chloride bands are shifted, and the bands become fainter with rise of temperature.

E. G.

Restoration of Phosphorescence to Sulphides of the Alkaline Earths. DÉSIRÉ GERKEZ (*Compt. rend.*, 1910, 150, 295—300).—Specimens of the phosphorescent sulphides of calcium, barium, and strontium were found to have lost their phosphorescence after an exposure of six years to moist air. This appeared to be due to oxidation to the sulphates, since the phosphorescence was restored by heating the substances in a current of hydrogen. The action of heat alone had very little effect on the phosphorescence.

W. O. W.

Photochemical Equilibria. III. Photochemical Equilibrium of Carbonyl Chloride. ALFRED COHEN and HANS BECKER (*Ber.*, 1910, 43, 130—133. Compare *Abstr.*, 1909, ii, 846).—Weigert (*Abstr.*, 1907, ii, 835) has found that the dissociation equilibrium of carbonyl chloride at 500° is not affected by light; the action of the latter is simply to accelerate catalytically the attainment of equilibrium. His experiments are not conclusive, however, since glass vessels were used. The authors now find that when carbonyl chloride is passed through a quartz tube at the ordinary temperature, and at the same time submitted to the action of light from a mercury-quartz lamp, it is partly decomposed into carbon monoxide and chlorine. When 1 c.c. of carbonyl chloride passed through the quartz

tube (20 cm. long and 0.5 cm. in diameter) per minute, the amount of decomposition was 3.3—4%. The effect is chiefly due to the short ultra-violet rays, since when tubes of Uviol glass were used, which are only transparent to waves of greater wave-length than 265μ , the decomposition was only 0.46—0.5%. In ordinary glass tubes there was no decomposition.

In all the cases hitherto examined, namely, the photochemical equilibria of sulphur trioxide, hydrogen chloride, and carbonyl chloride, the actual equilibrium is affected only by ultra-violet rays. Rays of greater wave-length simply act catalytically on the attainment of equilibrium.

Experiments which are at present in progress show that water vapour is decomposed to a considerable extent by ultra-violet light.

T. S. P.

Chemical Action of Light. V. Photochemical Phenomena in Dye Solutions. FRITZ WEIGERT (*Ber.*, 1910, 43, 164—172. Compare Abstr., 1908, ii, 5, 748, 914; 1909, i, 219, ii, 532).—In liquids exposed to the action of light, condensation nuclei are formed; these bring about local increases in concentration, and accelerate chemical reactions which do not take place in the dark. Proof of the formation of condensation nuclei is afforded by the fact that solutions of dyes exposed to light show an increased solvent action towards gases.

The dyes studied were uranin, erythrosin-G and -J, phloxin, methyl-violet, and malachite green. These were enclosed in tubes with nitrogen, maintained at 15°, and exposed to the light from a mercury lamp. A manometer was arranged to indicate the gas pressure in the tubes, which were constantly shaken. The solubility of nitrogen in water is not affected by exposure to light. In the dye solutions a decrease in pressure took place, at first with constant velocity, but subsequently becoming slower. After keeping the tubes in the dark again, an increase in pressure was found, but the original value was never attained. A special differential-adsorptionmeter was designed to remove the absorbed nitrogen by boiling the dye solution, but it was found only possible to recover a portion of the gas absorbed. The amount of dye present in solution is far too small to explain the increased solubility of the gas as due to the influence of the dye. Undoubtedly, condensation nuclei form, and the nitrogen condenses at their surface.

E. F. A.

Radioactivity of some Waste Springs in the Vosges. ANDRÉ BROCHET (*Compt. rend.*, 1910, 150, 291—293).—Near the thermal springs of Plombières, Luxeuil, and Bains, there exist in the region of the Vosges some springs running to waste. The radioactivity, both of the gases and water, of these springs has been found to be high. Particulars are given of springs of the Chaudeau, Fontaines-Chaudeas, and Chaudeas-Fontaines or Reherrey.

F. S.

Radioactivity of Halogen and Oxyhalogen Compounds of Thorium. J. CHAUDIER and EDOUARD CHAUVENET (*Compt. rend.*, 1910, 150, 219—221).—The radioactivity (α -radiation) of a number

of freshly prepared halogen and oxyhalogen compounds of thorium has been compared with that of thorium dioxide and thorium in a Curie electroscope. The powdered substances were sifted over plates 4 cm. in diameter, the weight of substance employed being varied up to 0.35 gram, for which the α -radiation is a maximum. In the latter case, the intensity of the radiation diminished as the atomic weight of the elements combined with the thorium increased. The substances arranged in descending order of activity were as follows: Th, ThO₂, ThOF₂, ThF₄, ThOCl₂, ThCl₄, ThOI₃, ThBr₄. As the weight of the substance employed is reduced, the differences in the relative activities of the compounds disappear. Below 0.01 gram all are of similar activity, indicating that the radioactivity is an atomic property of thorium.

F. S.

The Action of the α -Rays on Glass. ERNEST RUTHERFORD (*Mem. Manchester Phil. Soc.*, 1909, 54, v, 1).—Fine capillary tubes of soda-glass that had contained radium emanation show in transverse section a coloured region extending about 0.04 mm. from the inner wall of the capillary, corresponding with the range of the most penetrating α -rays of radium in glass. This confirms the correctness of Joly's explanation of pleochroic halos (*Phil. Mag.*, 1907, [vi], 13, 381; 1910, 19, 327).

F. S.

The Absorption Law of β -Rays. W. WILSON (*Physikal. Zeitsch.*, 1910, 11, 101. Compare *Proc. Roy. Soc.*, 1909, A, 82, 612).—The former conclusion, that the exponential law of the absorption of β -rays is indicative of non-homogeneity of the rays which have a certain distribution of velocities, is reaffirmed and the criticisms of Hahn and Meitner (this vol., ii, 8) are replied to in detail. The conclusion is drawn that the β -rays suffer diminution of velocity in passage through matter.

F. S.

Production of Helium by Radium. ERNEST RUTHERFORD and BERTRAM B. BOLTWOOD (*Mem. Manchester Phil. Soc.*, 1909, 54, vi, 1—2).—The gases generated in eighty-three days from a solution of a barium-radium salt containing 0.2 gram of radium, which had been freed chemically from polonium and radium-D, were subjected to repeated absorptions with charcoal cooled in liquid air, and the unabsorbed part was found to consist of helium, essentially pure, in amount corresponding with a rate of production of 163 cu. mm. per gram of radium per year. This is in very close agreement with the calculated rate (158 cu. mm.). Other experiments not described showed that helium is produced from polonium.

F. S.

The Accumulation of Helium in Geological Time. III. ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1910, A, 83, 298—301. Compare this vol., ii, 9).—The ratio of helium to uranium and thorium has been determined for zircons extracted from fourteen rocks ranging from Tertiary to Archean. Minerals like zircon and sphene contain hundreds of times as much helium as the average of the rock of which they are constituents, and accordingly the whole of the contained helium may be regarded as having been generated since the consolida-

tion of the rock and the separation of the mineral. The zircons were decomposed by fusion with borax in a platinum boat in a quartz tube filled with oxygen. The oxygen was removed from the extracted gas by phosphorus, leaving the helium. Each unit in the helium ratio (c.c. per gram of "total equivalent uranium oxide," 1 gram of thorium being reckoned equivalent in helium producing power to 0.203 gram of uranium oxide) is provisionally taken to indicate a period of eleven million years. The helium ratio of zircon stands in very close relation to the geological age of the specimen. For four specimens of the tertiary rocks the ratio is below unity, whilst for four specimens of paleozoic rocks the ratio is between 13 and 29. The oldest specimen from the archæan rocks of Canada has a helium ratio 56.6. These ratios fix the minimum values of the geological age, but in spite of the enormous lengths of time indicated it may be that the whole of the helium generated is not retained. The fraction retained, depending on the structure of the zircon, must be supposed, however, to be fairly definite, and similar for all. F. S.

Rate of Evolution of Heat by Pitchblende. HORACE H. POOLE (*Phil. Mag.*, 1910, [vi], 19, 314—326).—About half a kilogram of carefully dried powdered Joachimsthal pitchblende, containing 64% of uranium, was placed in a spherical Dewar vessel surrounded with ice, and, when a steady thermal state had been attained, the constant difference of temperature between the under-surface layer of the pitchblende at the bottom of the vessel and the ice outside was determined by means of thermocouples. The heat evolved per hour by the pitchblende was reckoned as the product of this constant difference and the thermal conductance of the calorimeter. The last, which was separately determined with water in the calorimeter, is the number of calories escaping from the calorimeter per hour when the inside is 1° hotter than the outside. To avoid chemical action, of which indications were obtained in the preliminary experiments in air, the calorimeter was filled with carefully dried nitrogen. The conclusion is drawn that 1 gram of the pitchblende evolved 6.1×10^{-5} calories per hour as a mean value of three experiments, the separate results being 7.1, 5.45, and 5.85 ($\times 10^{-6}$). The value is surprisingly high, the value calculated, presumably from the kinetic energy of the various α -particles expelled, being only about 4.4×10^{-5} for the sample of pitchblende employed. F. S.

The Emission of Positive Rays from Heated Phosphorus Compounds. FRANK HORTON (*Proc. Camb. Phil. Soc.*, 1909, 15, 329).—The object of the experiments was to test whether the large positive ionisation produced by heated phosphates, notably aluminium phosphate, observed by Sir J. J. Thomson had any connexion with the "anode rays" of Gehrcke and Reichenheim (*Abstr.*, 1908, ii, 343). The latter found most suitable the halide salts of the alkali and alkaline-earth metals, whereas the positive ionisation produced from these when heated is not nearly as great as from the phosphates. The salt, mixed with graphite to make it conduct, and sometimes with silver chloride to fuse the mass together, was rammed into a quartz tube and

strongly heated. The prepared tube was then mounted as anode with another electrode as cathode in an exhausted flask, and a discharge from a large coil passed. No "anode-rays" of the kind obtained from the halides of the alkali metals were obtained from the phosphates, but calcium phosphide and silver chloride did give such rays, the spectrum of their light showing the calcium and silver lines respectively. There is probably no connexion between the two phenomena in question. The experiments support Gehreke and Reichenheim's conclusions that the "anode rays" owe their origin to the electrolytic decomposition of the salt and expulsion of the metal from the anode into the vacuum. F. S.

Electrical Conductivity and Constitution of Dissolved Substances. S. W. SERKOFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 1—14 [Physical Part]. Compare Abstr., 1909, ii, 372).—According to the solvate theory (compare Jones, Abstr., 1909, ii, 221), a compound like lithium nitrate containing the ion Li, which undergoes intense hydration, should exhibit a well-marked maximum conductivity in mixtures of acetone with an alcohol, whilst potassium iodide should show no trace of a maximum conductivity. The author's conductivity curves are not in agreement with these conclusions. It is found, indeed, that potassium, sodium, and lithium iodides, which differ considerably in the extent of hydration which they undergo, show no maximum conductivity, whilst lithium bromide exhibits a maximum which is not very clearly marked, and lithium chloride a distinct maximum. Neither is there any parallelism observable between the sharpness of this maximum and the magnitude of μ_{∞} calculated by the ordinary method of extrapolation. Thus, for lithium chloride, $\mu_{\infty} = 63$, for lithium iodide $\mu_{\infty} = 181.0$, and for lithium bromide, $\mu_{\infty} = 144$. The influence of the formation of complex compounds on the molecular conductivity is discussed, and it is found that all the abnormal conductivity curves, corrected for the formation of complex compounds, exhibit characters determined by the corresponding fluidity curves. T. H. P.

Electrical Conductivity of Soap Solutions. JAMES W. MCBAIN and MILLICENT TAYLOR (*Ber.*, 1910, 43, 321—322).—A preliminary account of measurements of the conductivity of solutions of sodium palmitate. The measurements were made in silver vessels, with the following results:

Dilution in litres.....	1	1½	2	5	10	20	100
Mol. conductivity in mhos...	64.82	71.13	77.42	77.47	78.77	86.04	135.3

The results are compared with the conductivities of solutions of sodium hydroxide and sodium acetate, and show that the normal soaps do not exist as colloids in concentrated solution. T. S. P.

Diminution of Conductivity by Colloids and Observations relating to the Conductivity of Serum. WALTER FREI (*Zeitsch. Chem. Ind. Kolloide*, 1910, 6, 94—103).—The influence of serum-albumin, serum-globulin, gelatin, and saponin on the electrical

conductivity of a 0.5*N*-solution of sodium hydroxide at 37° has been examined. For 1% solutions of the four colloids, the conductivity is diminished to the extent of 7.5, 6.6, 5.5, and 5.6% respectively. The specific influence of a given colloid varies somewhat with the concentration. When the conductivity is plotted as a function of the concentration of the colloid, curves are obtained which are slightly convex towards the origin.

It is shown that the observed effects are in part due to phenomena of swelling and adsorption, which cause alterations in the concentration of the dissolved ions. In addition, the conductivity is diminished in consequence of a reduction of the cross-sectional area of the electrolytic solution by the colloidal particles, and also of the increase in the viscosity.

The simultaneous changes observed in the conductivity, freezing-point depression, viscosity, and density on dilution of solutions of serum are interpreted on the basis of the above considerations.

H. M. D.

Dielectric Cohesion of Neon. EDMOND BOUTY (*Compt. rend.*, 1910, 150, 149—150. Compare Abstr., 1904, ii, 309, 604).—The author has shown previously that the dielectric cohesions of the monatomic gases, helium, argon, and mercury vapour, are considerably less than those of polyatomic gases of comparable molecular weight. The dielectric cohesion of neon, obtained by fractionation of a gaseous mixture of neon, helium, and traces of air, is found to be 7.6, that of air being 43.5. It is considerably less than that of helium (18.3), although its value would be expected to lie between those of helium and argon. This is in agreement with the fact that Mendeleëff, in his last periodic table, places neon in a separate group from the other rare gases.

Attention is called to luminous effects observed when the pressure on neon is diminished by means of a mercury pump.

T. S. P.

Thermodynamics of Standard Cells. ERNST COHEN and HUGO R. KRUYT (*Chem. Weekblad*, 1910, 7, 69—78).—A criticism of Hulett's calculation of the chemical energy of the Weston standard cell (*Trans. Amer. Electrochem. Soc.*, 1909, 15, 435).

A. J. W.

Electrochemical Equivalent of Silver. F. LAPORTE and P. DE LA GORCE (*Compt. rend.*, 1910, 150, 278—280).—Improvements introduced into the purification of silver nitrate have brought the authors' earlier results into better agreement with those obtained at the National Physical Laboratory and elsewhere. Crystallisation of the salt between 30° and 40°, under reduced pressure and in the absence of air, gave, as a mean of eight experiments, 1.11827 mg. per Coulomb as the electrochemical equivalent of silver. As a mean between this and other results, the authors adopt 1.11829 mg. as correct. It is important that the air to which the solutions of silver nitrate are exposed should be free from impurities. In one experiment in which tobacco smoke was present, a high result was obtained.

W. O. W.

Correction for the Method of Determining Galvanic Ennobling of Metals. CHARLES M. VAN DEVENTER and H. J. VAN LUNNEL (*Zeitsch. physikal. Chem.*, 1910, 71, 117—127).—In connexion with the experiments on the galvanic ennobling of metals already described (compare Abstr., 1908, ii, 12, 558; 1909, ii, 958), it has been found necessary to apply a correction for the alteration of the surfaces of the metals during the experiment. This has been done by comparing the potentials of the two metals in acid before and after the "ennobling" experiment. The application of this correction does not greatly alter the results already given. Thus as regards cadmium, lead, tin, nickel, and amalgamated zinc, one electrode can be ennobled with regard to another of the same metal, and for the following pairs of metals, zinc-cadmium, tin-lead, zinc-tin, cadmium-tin, and lead-nickel, the first metal can readily be ennobled with reference to the other. G. S.

Electrolysis of Molten Salts. RICHARD LORENZ (*Festschrift Otto Wallach*, 1909, 513—539).—An account is given of the chief results obtained in recent investigations on the electrolysis of molten salts. The possibility of explaining the observed facts in terms of the theory of electrolytic dissociation is discussed. H. M. D.

Magnetisable Alloys of Manganese. FRIEDRICH HEUSLER (*Festschrift Otto Wallach*, 1909, 467—477. Compare Abstr., 1909, ii, 541).—Polemical against Wedekind. A summary is given of the chief results of work already published in connexion with the magnetic properties of manganese copper-aluminium alloys. H. M. D.

Magnetic Measurements of Platinum Metals and of Monoclinic Crystals, in Particular of Iron, Cobalt, and Nickel Salts. WILHELM FINKE (*Ann. Physik*, 1910, [iv], 31, 149—163).—Measurements have been made of the magnetic susceptibility of platinum, palladium, iridium, and rhodium, and also of ferrous sulphate, nickel sulphate, cobalt sulphate, ferrous ammonium sulphate, nickel ammonium sulphate, cobalt ammonium sulphate, cobalt potassium sulphate, cobalt copper sulphate, epidote, augite, hornblende, adularia, and sucrose.

For the isotropic metals, the susceptibilities are: platinum, $+22.6 \times 10^{-6}$; palladium, $+66.26 \times 10^{-6}$; iridium, $+4.89 \times 10^{-6}$; rhodium, $+12.58 \times 10^{-6}$. In the case of the monoclinic crystals no connexion could be traced between the position of the magnetic axes on the one hand and that of the optic and di-electric axes on the other. H. M. D.

Use of the Magnetic Field as a means of Determining Constitution in Organic Chemistry. IV. PAUL PASCAL (*Bull. Soc. chim.*, 1910, [iv], 7, 45—51. Compare Abstr., 1909, ii, 487, 788, 859, and this vol., ii, 100).—In this paper the anomalous magnetic susceptibilities shown by halogenated and cyano-compounds are considered, and it is shown that the apparent departure from the simple

additive character of this constant is due in the case of haloid derivatives to (1) mutual action of a hydrogen and a halogen atom, and (2) mutual action of halogen atoms, and in the case of cyano-derivatives to the acid character conferred by the cyano-group.

In the case of simple alkyl haloids, the diamagnetic deficit for the whole molecule amounts to about 32×10^{-7} for monochloro-derivatives and to 42.5×10^{-7} for monobromo- and moniodo-compounds. For symmetrical dichlorides, it is about 45×10^{-7} , and for dibromides about 60×10^{-7} . Where the two chlorine atoms are attached to the same carbon atom, the deficit is about 67×10^{-7} in open-chain compounds, but it is less where the carbon is attached to a benzene nucleus, thus for CHPhCl_2 it is 42.5×10^{-7} .

In cyano-compounds the diamagnetic excess is about 45×10^{-7} for benzonitrile, phenylacetoneitrile, or ethyl cyanoacetate, and is of about the same order as in the mineral acids.

T. A. H.

Conduction of Heat through Rarefied Gases. FREDERICK SODDY and ARTHUR J. BERRY (*Proc. Roy. Soc.*, 1910, A, 83, 254—264).

—The heat dissipated from a bright platinum strip maintained by a current at 61° in various gases has been measured by an electric method at various pressures down to a thermally perfect vacuum. The process of producing high vacua by means of the vapour of calcium was employed. At pressures such that the actual path of the gas molecule is comparable with its mean free path, the heat dissipated is proportional to the pressure of the gas. The conductivity under these conditions bears no relation to the ordinary conductivity at higher pressures, where the conductivity is independent of pressure. The conductivity of acetylene, methane, and cyanogen slightly exceeds that of hydrogen, whilst helium conducts but slightly better than carbon dioxide. In the table, the second column represents the ordinary conductivity of the gases as expressed by the watts dissipated by a definite portion of the strip at pressures above which the conductivity does not further increase with pressure. The third column (\bar{K}) indicates the found values of the conductivity at low pressure, expressed as the calories ($\times 10^{-5}$) dissipated per cm^2 of surface, per 0.01 mm. pressure per 1° difference of temperature. The fourth column (Q) is the value for this conductivity calculated from the kinetic theory on the assumption that the heat interchange at impact is perfect. The last column shows the ratio of K to Q .

	Watts.	K .	Q .	K/Q .
Argon.....	1.07	1.30	1.20	1.09
Neon	2.35	1.76	1.70	1.04
Carbon dioxide.....	0.95	1.59	2.64	0.72
Oxygen	1.55	1.91	2.23	0.86
Helium	7.30	1.94	3.80	0.51
Carbon monoxide.....	1.37	1.96	2.38	0.82
Nitrous oxide	0.97	2.11	2.75	0.77
Nitrogen	1.44	2.21	2.35	0.94
Hydrogen	8.75	2.29	8.95	0.25
Cyanogen	0.97	2.35	—	—
Methane	2.81	2.70	3.95	0.68
Acetylene	1.24	2.75	3.82	0.72

The results indicate a method of obtaining information concerning the nature of the single impact of a molecule on a surface. The interchange of energy appears perfect for the denser monatomic gases, but for the more rapidly moving molecules of helium and hydrogen this is far from the case. In such cases at low temperatures, or for hydrogen if a palladium instead of a platinum surface were used, the conductivity ought to be increased, owing to more perfect interchange of energy on impact.

F. S.

Heat Capacity of Certain Metals and Compounds of Metals. HERMANN SCHIMPF (*Zeitsch. physikal. Chem.*, 1910, 71, 257—299).—The specific heats of fifteen metals and twenty-nine binary compounds of metals have been determined by the method of mixtures for the three temperature intervals 17 to 100°, 17 to -79°, and 17 to -190°. As the metallic compounds were mainly prepared in the course of the investigations on alloys by Tammann and his pupils, they may be regarded as of well-defined composition. From the results, the mean specific heats at +50°, 0°, -50°, -100°, and -150° are calculated, and are given in tabular form. The limit of experimental error is about 1%.

The mean specific heats of the metals for the three temperature intervals 17 to 100°, 17 to -79°, and 17 to -190° are as follows: Magnesium, 0.2475, 0.2284, 0.2046; aluminium, 0.2173, 0.1976, 0.1696; silicon, 0.1753, 0.1470, 0.1166; chromium, 0.1102, 0.0980, 0.0805; iron, 0.1098 (17 to 100° only); nickel, 0.1088, 0.0974, 0.0830; cobalt, 0.1030, 0.0942, 0.0818; copper, 0.0925, 0.0880, 0.0786; zinc, 0.0934, 0.0886, 0.0819; silver, 0.0580, 0.0544, 0.0506; tin, 0.0556, 0.0521, 0.0488; antimony, 0.0503, 0.0482, 0.0450; gold, 0.0310, 0.0297, 0.0283; platinum, 0.0310, 0.0293, 0.0286; bismuth, 0.0303, 0.0285, 0.0275. The results are compared in detail with those of previous observers, and in the majority of cases the agreement is satisfactory.

For about half the compounds, the specific heats are equal to the sum of the specific heats of the component metals with a maximum deviation of 2%; in the other cases the deviations from Kopp's rule are, in general, within 4%. It is remarkable that in all cases the observed specific heats of the magnesium compounds are smaller, and in most cases those of the antimony compounds greater, than the values calculated according to Kopp's rule.

A formula with three constants is suggested to represent the variation of the specific heats with the temperature between +50° and -150°, and the respective constants for each metal and compound are calculated from the above observations. In all cases the specific heat increases with the temperature, but, except for bismuth and lead, the magnitude of the temperature-coefficient diminishes as the temperature rises. The observations afford no definite information as to the variation of the specific heats above +50° and below -150°.

As regards the atomic heats of the free metals, the average values, excluding silicon, are 4.56, 5.13, 5.60, 5.93, and 6.13 at -150°, -100°, -60°, 0°, and 50°, and the mean values for the metals in combination are 4.24, 4.89, 5.40, 5.75, 5.95 at the same temperatures.

G. S.

Specific Heat of Metallic Alloys. ALEXIS V. SAPOSHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1708—1711).—In order to test Regnault's law, according to which the specific heat of an alloy is equal to the mean arithmetic specific heat of its components (*Ann. Chim. Phys.*, 1841, [iii], 1, 129), the author has determined the specific heats at 15—100° of alloys of various compositions of (1) bismuth and cadmium, which form neither compounds nor solid solutions; (2) lead and tin, which do not give compounds and only form solid solutions of low concentrations; (3) bismuth and antimony, which form an uninterrupted series of solid solutions; and (4) zinc and antimony, which form the two compounds SbZn and Sb_2Zn_3 . In all cases, Regnault's law is confirmed within the limits of experimental error, so that the specific heat of an alloy is an additive property.

T. H. P.

Melting-Point Determinations at Low Temperatures. II. STOLTZENBERG (*Chem. Zeit.*, 1910, 34, 66—67).—The author describes a modification of his melting-point apparatus for low temperatures (this vol., ii, 17). The tube into which the thermometer dips is double walled, the space between the walls being evacuated.

T. S. P.

Measurement of the Heats of Liquefaction of Acetic Acid, Benzene, and Nitrobenzene. JULIUS MEYER (*Festschrift Otto Wallach*, 1909, 540—568).—The author has measured the thermal and volume changes which accompany the liquefaction of benzene, nitrobenzene, and acetic acid. Both series of measurements were made with apparatus resembling the Bunsen ice calorimeter. The mean values obtained for the heats of liquefaction are benzene 30.39, nitrobenzene 22.53, acetic acid 45.96 cal. From these data and the observed melting points (5.44°, 5.82°, and 16.54°), the respective molecular freezing-point lowerings are found to be 5.059, 6.849, and 3.621.

The increments of volume on liquefaction of one gram of substance amount to 0.1333, 0.0808, and 0.1578 c.c. respectively. From these data the influence of pressure on the melting point is calculated. The rise of temperature per atmosphere pressure amounts to 0.0295°, 0.0242°, and 0.0241° for benzene, nitrobenzene, and acetic acid respectively, and in all cases these values are found to be in satisfactory agreement with the experimental determinations.

H. M. D.

Chloroacetic Acid as a Cryoscopic Solvent. EFISIO MANERI (*Gazzetta*, 1909, 39, ii, 579—586).—Of the various modifications of chloroacetic acid, only the most stable or α -form gives good results as a cryoscopic solvent (compare Tanatar, *Abstr.*, 1893, i, 624; Hulett, *Abstr.*, 1899, ii, 468). The mean of the results obtained with xylene, *m*-cresol, saffrole, and acetic acid in concentrations not greater than 3% gives the value 52 for the cryoscopic constant of chloroacetic acid, the number calculated by means of van't Hoff's formula being 54.19. Neither the α - nor β -modification of chloroacetic acid forms solid solutions with acetic acid, both giving normal molecular weights in this solvent.

The molecular weight of water in freezing chloroacetic acid is slightly above the normal value at low concentrations, and about 1.5 times the calculated value for a 12% solution. With phosphoryl chloride the molecular weight is less than the normal at low concentrations and increases with the concentration, the calculated value being passed at about 1.3%.

With aniline, pyridine, and quinoline, chloroacetic acid behaves as a slightly dissociating solvent, the molecular weights being somewhat lower than the normal values, even for very dilute solutions, and decreasing gradually as the concentration increases.

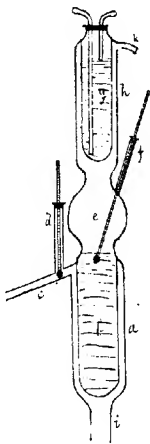
T. H. P.

A New Fractionating Column. ALFRED HAIN (*Ber.*, 1910, 43, 419—423).—The principle of the column is that the vapour from the boiling liquid passes through a space which is kept at a constant temperature, but, nevertheless, can absorb heat readily. The details of the apparatus will be readily understood from the diagram. The constant temperature in the narrow space, *a*, through which the vapour of the boiling liquid passes, is maintained by the boiling liquid in *b*. This latter liquid must be chosen to give a suitable temperature, and its boiling point may be altered by connecting *k* with a water pump; *g* is a condenser for the liquid boiling in *b*.

With this apparatus the distillate from a 45% alcohol consisted of 96% alcohol, the liquid in *b* being at 76°; other fractionating columns gave a 92—93% distillate. Mixtures of ether and alcohol, methyl and ethyl alcohols, and of methyl ethyl ketone (b. p. 81°) and diacetyl (b. p. 87°) were satisfactorily separated.

The apparatus possesses the great advantage that it does not require continual watching.

T. S. P.



An Apparatus for the Measurement of the Vapour Pressures of Dilute Aqueous Solutions. RUDOLF MATER (*Ann. Physik*, 1910, [iv], 31, 423—435).—An apparatus has been devised by means of which the small differences between the vapour pressures of water and dilute aqueous solutions can be measured with considerable accuracy. The arrangement is such that absolute measurements of small vapour pressures can also be made.

The mercury manometer consists of a U-shaped tube, supported firmly on a stand provided with levelling screws. A fine platinum-iridium point is supported in each arm of the tube, and contact of these with the mercury is indicated electrically. Each of the supports, to which the platinum-iridium needles are attached, is capable of vertical movement, the amount of which is measured by means of a micrometer screw.

Another essential feature of the apparatus is the special arrangement adopted for ensuring that the two liquids shall have the same temperature. This consists of a double vessel, the inner and outer parts of which are connected with tubes leading to the manometer by carefully ground glass joints. The inner vessel, in which the water is placed, is of platinum, which facilitates the attainment of thermal equilibrium between its contents and the solution which surrounds it.

The data obtained in experiments with solutions of sucrose in water at 0° are recorded. The vapour-pressure differences thus found are in good agreement with those calculated from Raoult's vapour-pressure equation.

H. M. D.

Partial Pressures of Liquid Mixtures. WILLIAM E. STORY (*Zeitsch. physikal. Chem.*, 1909, 71, 129—151).—A mathematical paper. The Duhem-Margules equation, which refers to the vapour pressures of the components of a binary mixture, has been extended to mixtures with any number of components, and a general solution of the equation is given. It is shown that Raoult's law can be deduced directly from the Duhem-Margules formula, and that the latter formula is based on no other assumptions than those comprised in Raoult's law. The series containing the solution of the equation are more convergent than those hitherto used. The methods of deducing the coefficients of the formulæ from the experimental data are discussed in detail.

G. S.

Binary Mixtures and Concentrated Solutions. II. FRIEDRICH DOLEZALEK (*Zeitsch. physikal. Chem.*, 1910, 71, 191—213. Compare Abstr., 1909, ii, 22; Bein, *ibid.*, 471; Möller, *ibid.*, 981).—The theory of the vapour-pressure of binary mixtures described in the previous paper is illustrated by further examples, and is extended to other properties of these mixtures.

From the total vapour-pressure curve of mixtures of ethyl ether and chloroform, as determined by Guthrie (Abstr., 1885, 339), the partial vapour-pressure curves of the components are deduced, and it is shown that the components enter into combination in molecular proportions. At 19°, when the components are present in equimolar proportions, the mixture contains 24 mol. % of the compound. The view that a compound containing one molecule of each of the components is formed is further supported by the fact that the heat of admixture, and the contraction on mixing, both attain a maximum value when the components are present in equivalent proportions.

Similarly, from the determination by Inglis (Abstr., 1906, ii, 332) of the partial pressures of nitrogen and oxygen above mixtures of the liquefied gases, it is shown that liquid nitrogen is non-associated and liquid oxygen associated. At 74.7° abs., in a mixture of liquefied oxygen and nitrogen in molar proportions, there is about 1 mol. O₂ for every 7 mols. O₂, and in pure oxygen 1 mol. O₂ for 3.03 mols. O₂. At 79.07° there is 1 mol. O₂ for 4.53 mols. O₂, and above 86° abs. oxygen exists only as simple molecules.

The application of the theory to the solubility of a gas in a liquid, on the assumption that the system is a highly concentrated solution of

the liquid in the liquefied gas, leads to the expression: $p/p_0 = q$, where p is the partial pressure of the gas, and p_0 is the vapour pressure of the liquefied gas (in the unimolecular form) at the same temperature. Hence, if the same gas is dissolved at the same pressure and temperature in different liquids, p and p_0 , and, therefore, q , have the same values throughout; the solubility of a gas, expressed as a true molar fraction, should be the same for all chemically indifferent liquids. This deduction is shown to be approximately valid for the solubility of carbon dioxide in benzene, chlorobenzene, bromobenzene, and chloroform when for p_0 the corrected pressure $p_0 + a/v^2$, in the sense of van der Waals, is used. The applicability of the method is limited by the fact that at the temperatures at which solubilities are usually measured, the permanent gases are far above their respective critical temperatures.

Further, the theory leads to the result that the ratio of the solubilities of two indifferent gases should be the same for different solvents, provided that the molecular weights of the solvents are not greatly affected by dissolving the gases in them. This law has already been discovered experimentally by Just (Abstr., 1901, ii, 439).

The expansion of a liquid produced by dissolving a gas in it has also been calculated, and the observed and calculated values are in good agreement. Finally, the thermal phenomena observed on admixture of liquids are also satisfactorily represented by the theory.

G. S.

Experimental Determination and Thermodynamic Calculation of the Vapour Pressures of Toluene, Naphthalene, and Benzene. JONATHAN T. BARKER (*Zeitsch. physikal. Chem.*, 1910, 71, 235—253).—The vapour pressures of toluene through a wide range of temperature, of liquid and solid naphthalene, and of solid benzene have been determined by the dynamical method, a current of oxygen being saturated with the organic vapour, and the amount of the latter carried over determined by combustion. Various arrangements for securing saturation of the oxygen are described. The method proved satisfactory down to vapour pressures equal to 0.005 mm. of mercury.

The vapour pressures of toluene, in mm. of mercury at 0°, are as follows: 0.0054 at -78°, 1.61 at -21°, 16.8 at 14.8°, 28.75 at 25.8°; of naphthalene, 0.064 at 20°, 0.164 at 30°, and 0.378 at 40°; and of benzene, 0.0180 at -77.5°. Data for these substances at other temperatures are already available.

The object of the determinations was to test the vapour-pressure formula of Nernst: $\log p = -\lambda_0/4.571T + 3.5/R \cdot \log T - \epsilon/T + C$, where λ_0 , ϵ , and C are constants related in a definite way to the properties of the substance. The formula represents the experimental results satisfactorily. The calculated molecular heat of vaporisation of toluene at 111° is 7775 cal. as compared with the experimental values 7687 cal. (Schiff) and 8044 cal. (Campbell Brown). The latent heat of fusion of naphthalene (calculated) is 4435 cal. per mol., in good agreement with the experimental value. The calculated heat of vaporisation of solid benzene is 10,220 cal. per mol.; it has not been determined directly. The calculated heat of fusion of benzene,

1900 cal. per mol., does not agree very satisfactorily with the mean of the experimental values, 2326 cal. G. S.

Corresponding States. KIRSTINE MEYER née BJERRUM (*Zeitsch. physikal. Chem.*, 1910, 71, 325—336).—In a previous paper (Abstr., 1900, ii, 263) it was pointed out that van der Waals' theory of corresponding states is not strictly applicable, but that a good agreement between theory and experiment is observed when for each substance a special minimum temperature and minimum volume is calculated, and different units of pressure, volume, and temperature are used. In this way a common vapour-pressure curve for twenty-five substances has been obtained with the ordinate $y = (P_c - P)/P_c$ and abscissa $x = (T_c - T)/K$, where K is a temperature constant and the other symbols have the usual significance. It is now shown, mainly by means of data due to Young, that octane, diisopropyl, diisobutyl, and hexamethylene, as well as chlorine and carbon dioxide, follow the law fairly accurately.

In the former paper, T_{min} was taken as zero for fluorbenzene, and other substances were referred to this arbitrary value. In order to give K a more definite meaning, hydrogen is now chosen as reference substance, so that K represents the difference between the critical temperature of the substance T_c and the lowest temperature, T_{min} , at which the substance can exist in the gaseous condition, the assumption being made that this is true for hydrogen in the neighbourhood of the absolute zero. On this basis it is shown, from the data of Ramsay, Travers, Olszewski, and others, that nitrogen and the gases of the argon series follow the law, and the values of $T_{min} = T_c - K$ are calculated for a large number of substances.

When helium is chosen as the reference substance, for which T_{min} is zero, T_{min} for hydrogen becomes 7.9, but the values for T_{min} calculated on this basis for other substances are too high, a result due to the uncertainty as to the critical temperature and other data for helium. G. S.

Laws of Evaporation. PIERRE VAILLANT (*Compt. rend.*, 1910, 150, 213—216. Compare Abstr., 1908, ii, 460; 1909, ii, 544).—The supposition has been advanced that the rate of evaporation of an aqueous solution depends solely on the rate of diffusion of aqueous vapour out of a layer of saturated air in the immediate neighbourhood of the surface. This is supported by the observation that when the solution is contained in a vessel with an opening of known area, the quantity of liquid evaporated per second (Q) is not proportional to S , the area of the opening, but is a function of S independent of the nature of the liquid. It has also been shown, that in the case of an incompletely filled, straight-walled vessel, the speed of evaporation is governed by the formula $Q = aMF^{4/3}$, where M denotes the molecular weight of the liquid and P its vapour tension, whilst a is a constant almost independent of the nature of the liquid. Eighteen liquids have been studied, including water, carbon disulphide, hydrocarbons, alcohols, ethers, and organic halogen derivatives; the results are given in tabular form. W. O. W.

Thermochemical Investigations of Organic Compounds. IV—VII. Sulphur, Halogen, and Unsaturated Compounds. W. ŚWIĘTOSŁAWSKI [SVENTOSLAVSKY] (*Bull. Acad. Sci. Cracov*, 1909, 941—972. Compare Abstr., 1909, ii, 23, 213, 547).—The analysis of thermochemical data is extended to compounds containing sulphur and the halogens and to unsaturated compounds.

From the data for mercaptans and sulphides, the conclusion is drawn that the heat of formation of the linking C-S is greater in the sulphides than in the corresponding mercaptans. This result is the same as that found in the case of ethers and the corresponding alcohols.

Although the data for halogen compounds have not been accurately determined, the numbers obtained by different observers exhibiting considerable divergence, the heats of formation of the linkings C-Cl, C-Br, and C-I appear to be regulated by the same laws as those which govern the heat quantities associated with the linkings between carbon and other univalent groups.

From the data for unsaturated compounds, the conclusion is drawn that the minimum value of the heat of formation of the linking C-C is about 18.0 Cal.

By means of the equations which express the thermochemical values of the linkings between carbon and other elements and between hydrogen and other elements, the heat changes corresponding with the equation $(C-X) + (H-Y) = (C-Y) + (H-X)$ are calculated, X and Y representing any of the elements: carbon, hydrogen, oxygen, nitrogen, sulphur, chlorine, bromine, and iodine.

H. M. D.

Andrews' Measurements of the Compression of Carbon Dioxide and of Mixtures of Carbon Dioxide and Nitrogen. C. G. KNOTT (*Proc. Roy. Soc. Edin.*, 1909, 30, 1—22).—The data obtained by Andrews in his classical experiments on the compressibility of carbon dioxide are tabulated in compact form. Similar data are also recorded for mixtures containing nitrogen and carbon dioxide in the volume ratios 1:3.43 and 1:6.2. These data have been collected partly from the memoirs published in 1869, 1876, and 1886, and partly from note-books left by Andrews.

H. M. D.

Dependence of the Cubic Compressibility of Potassium and Sodium on the Temperature. LUDWIG PROTZ (*Ann. Physik*, 1910, [iv], 31, 127—148).—By means of thermodynamic reasoning it can be shown that the difference between the specific heats of a substance at constant pressure and at constant volume is dependent on the compressibility of the substance. With the object of obtaining information in regard to the variation of this difference with the temperature, the author has measured the compressibility of potassium and sodium at different temperatures.

The piezometric arrangement used in the experiments was similar to that described by Röntgen and Schneider. Measurements of the compressibility of water and petroleum were made in the first instance, the data for water being utilised in the calibration of the apparatus,

and those for petroleum in connexion with the compressibility of the solid metals. The experimental results show that the compressibility of potassium, sodium, and petroleum increases with the temperature according to a linear equation. From this it follows that the difference between the two specific heats increases with the temperature in the case of the two alkali metals.

In the case of water, a minimum compressibility is found at about 60°. H. M. D.

Condensation of Water by Electrolytes. FRANK K. CAMERON and WILLIAM O. ROBINSON (*J. Physical Chem.*, 1910, 14, 1—11).—The densities of solutions of certain acids, bases, and salts, in concentrations varying from $N/10$ to $N/200$, have been carefully determined at 25° by a pycnometer method, and from the results the amount of water "condensed" by a mol. of each electrolyte has been calculated on the assumption that the latter retains its volume in the anhydrous form unchanged in solution. The results do not show any very definite regularities. Substances which show large heats of solution or have a tendency to crystallise with water of crystallisation have relatively high condensing power. The specific condensing power usually diminishes with increased concentration, but for hydrochloric and nitric acids the condensation increases at first with the concentration, attains a maximum in approximately 1% solution, and beyond that point diminishes. The results of previous observers on this subject are summarised. G. S.

A Method of Determining the Viscosity of Gases, especially those available only in Small Quantities. A. O. RANKINE (*Proc. Roy. Soc.*, 1910, A, 83, 265—276).—The apparatus, which has been designed for measurements of viscosity with small quantities of gases, consists of two parallel tubes connected at both ends. One of the tubes consists of a very fine capillary, the other being of much greater cross-sectional area, yet sufficiently narrow for a pellet of mercury to remain intact inside it. Taps are provided above and below for the purpose of cleaning the tubes and filling the apparatus with gas. The rate of fall of the mercury pellet in the wider tube is determined by the viscosity of the gas which is forced through the capillary tube as the mercury descends. The formula from which the viscosity is calculated is $\eta = \pi R^4 p t / 8 l v$, in which R is the radius of the capillary tube, l its length, p the difference of pressure on the two sides of the mercury, v the volume of gas forced through the capillary, and t the time of fall. On account of capillary attraction, the value of p is not proportional to the length of the pellet of mercury, but it is shown that the capillary effect can be eliminated by using different lengths of mercury.

The apparatus was used for determining the viscosity of dry air at different temperatures. The absolute values at 11.2°, 15.5°, and 19.2° are respectively 1.770 , 1.803 , and 1.828×10^{-4} .

It is proposed to use the apparatus for the examination of neon, xenon, and krypton. For observations at high pressures, the method

described is much simpler than those which have been previously used. On the other hand, it is not suitable for work at low pressures.

H. M. D.

Torsional Elasticity and its Connection with Viscosity. O. FAUST and GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1910, 71, 51—58. Compare Lauer and Tammann, *Abstr.*, 1908, ii, 667).—The elasticity measurements were made by the method already described (*loc. cit.*); the viscosity measurements were taken from available data, and in a few cases were made by the usual time of flow method. Data for twenty-five liquids are given. For liquids of high viscosity there was only one back movement after the impulse and then a slow movement to the null position; for those of smaller viscosity unsymmetrical swinging about the null position; both phenomena indicate the existence of torsional elasticity. For those with still less viscosity, the swinging was symmetrical about the null position, indicating absence of torsional elasticity.

Viscosity and torsional elasticity are directly proportional. For all substances with a viscosity less than 4.3×10^{-2} , no torsional elasticity was observed under the experimental conditions, but all substances with a viscosity greater than 8.6×10^{-2} showed the above property. The ratio of the single backward movement to the movement produced by the impulse increases with the viscosity, and even exceeds unity for liquids of the highest viscosity. The magnitude of the viscosity at which torsional elasticity becomes marked depends on the sensitiveness of the measuring apparatus.

The proportionality between viscosity and elasticity has also been shown by allowing certain liquids to cool slowly and determining the viscosity at which torsional elasticity can just be detected by a very sensitive method. In all cases it appears at approximately the same value of the viscosity.

Certain viscous liquids become doubly refracting under stress, and it is shown from the data of previous observers that for castor oil the magnitude of the forced double refraction alters with the temperature proportionally to the viscosity.

G. S.

Absorption of Liquids by Porous Substances. J. H. RUSSENBARGER (*Compt. rend.*, 1910, 150, 275—278).—The “absorptive power” of a substance may be determined by suspending a thread of the material at one end of a wire passing over a pulley. The thread dips in water, which rises to a height h , and a weight, p , is attached to the other end of the wire to secure equilibrium. The author develops the following expression to represent the absorptive power: $X = \frac{p}{QS} \cdot \frac{dh}{dt} = \frac{h}{Q} \cdot \frac{dh}{dt}$, where S is the area of the cross section of the thread, Q the weight of absorbent material in unit-volume, and dh/dt denotes the speed at which the water rises. It is found by experiment that for the same kind of material, X is approximately constant.

By integration $h^2 = 2QXt + C$. It is, therefore, only necessary to

measure the height to which water rises in a thread of cotton held between two glass plates, to have a measure of its absorptive power.

W. O. W.

Three-phase Equilibrium (with a Pressure Minimum) of a Dissociating Compound of Two Components. III. GERARD H. LEOPOLD (*Zeitsch. physikal. Chem.*, 1910, 71, 59—89. Compare Abstr., 1908, ii, 218, 472).—The complete equilibrium between aniline hydrochloride and its components has been investigated.

The m. p. of aniline hydrochloride is $199.2-199.3^{\circ}$, and at this temperature it is only very slightly dissociated. The freezing-point curve of the system aniline-hydrogen chloride has been determined, and no evidence of the existence of a compound other than the above has been obtained.

Within certain narrow limits, aniline hydrochloride and hydrogen chloride are not completely miscible; the lowest temperature at which this occurs is 10.5° , the mixture containing 5.3 mol.% of aniline, and the highest temperature 51.1° , which is the critical temperature of the upper liquid layer and the vapour. This critical temperature is very slightly lower ($0.15-0.20^{\circ}$) than that of pure hydrogen chloride.

The mixture of maximum boiling point at atmospheric pressure contains about 51 mol.% aniline. The b. p. of aniline hydrochloride itself cannot be determined in the ordinary way, as part of the hydrogen chloride at once escapes, and the constant boiling mixture is obtained; the boiling point of the latter is 244.4° . The boiling-point curve of mixtures of the constant-boiling liquid and aniline has also been determined.

The boiling-point curve for a lower pressure has also been deduced by construction from the three-phase curve and the melting-point curve; in this case the maximum occurs in a mixture containing 50.8 mol.% of aniline.

The vapour-pressure curve of aniline hydrochloride has been determined. In this case the melting point occurs, as already mentioned, at 199.2° , and a vapour pressure of 19.4 cm., whilst the maximum sublimation point occurs at 198° and a pressure of 16.2 cm.

Finally, the three-phase curves have been determined for mixtures containing excess of aniline and of hydrogen chloride respectively in the liquid phase. In the curve of the former system there is a maximum at 175° and 29.2 cm. pressure, and a minimum at 197.5 and 16.0 cm. pressure. The maximum for mixtures containing excess of hydrogen chloride could not be measured directly, owing to the high pressure, but other parts of the curve have been determined.

G. S.

Relation between Density and Degree of Dissociation of Aqueous Salt Solutions. S. TERESCHIN (*Ber. Deut. physikal. Ges.*, 1910, 12, 50—53).—The author has shown previously (Abstr., 1909, ii, 552) that the constant A_s of Heydweiller's formula (*Ber. Deut. physikal. Ges.*, 1909, 11, 37) may be regarded as the sum of two moduli, each belonging to one of the ions and independent of the nature of the

other ion. By means of Heydweiller's further results (this vol., ii, 106), the author shows that these density moduli are subject to certain laws. Thus, the moduli of the elementary ions increase proportionally to the atomic weight in the separate groups of the periodic system. The magnitude of the water envelope surrounding the ion is doubtless related closely to the density modulus (compare Kohlrausch, Abstr., 1902, ii, 489). Possibly the irregular position occupied by fluorine as regards its mobility and the temperature-coefficient of the latter, in comparison with the other members of the halogen group (Kohlrausch, *loc. cit.*), is to be attributed to the abnormal magnitude of its density modulus, which is considerably higher than it should be according to the straight line curve between the moduli and atomic weights.

T. H. P.

Behaviour of Aqueous Solutions in Capillary Actions. ZDENKO H. SKRAUP (*Monatsh.*, 1909, 30, 773—824).—The present communication contains the results of a large number of observations made with acids, bases, and salts of the most varied character; it is not yet possible to make strictly accurate generalisations, although the statements made previously (Abstr., 1909, ii, 868) receive further support from the results of the extended inquiry. The following are the most striking results not published hitherto: (1) In equivalent and extremely dilute solutions, strong bases ascend higher than strong acids. (2) Phosphoric acid, although a relatively weak acid, does not ascend to the same height as the strongest acids. (3) In general, salts ascend much higher than the acids or bases, in equivalent solutions, of which they are formed; in many cases the salt rises to practically the same height as the water. (4) Sucrose and antipyrine, in all degrees of dilution, ascend to the same height as the water. (5) Colloidal ferric hydroxide, in strong solutions, appears to retard the ascent of water.

Observations, similar to those made with filter paper, have been made with silk, wool, and plates of unglazed porcelain and plaster of Paris.

W. H. G.

Diffusion and the Kinetic Theory of Solutions. J. THOVERT (*Compt. rend.*, 1910, 150, 270—272. Compare Abstr., 1903, ii, 13).—The relation between the molecular weight, M , and the diffusion coefficient, D , of a substance in solution has been represented by the formula $D\sqrt{M}=C$, where C is a constant. For a large number of substances it has been shown that $C=12\times 10^{-3}$; it is now found, however, that in many cases C may have a much larger value. Compounds of similar structure usually show the same value for C . An explanation, based on the kinetic theory, is put forward to account for these observations.

W. O. W.

Action of Membranes. HEINRICH BECHHOLD and J. ZIEGLER (*Zeitsch. Chem. Ind. Kolloide*, 1910, 6, 122—123).—The authors object to the view put forward by Liesegang respecting the nature of precipitation membranes. In the case of the membrane which is formed when equimolecular solutions of sodium chloride and silver

nitrate in gelatin are allowed to diffuse towards one another, a condition of statical equilibrium is set up. After the formation of the membrane, no further reaction between the two substances can be observed.

H. M. D.

Properties of Solutions at their Critical Solution-Temperatures. A. N. SCHÜKAREFF (*Zeitsch. physikal. Chem.*, 1910, 71, 90—108. Compare *ibid.*, 1897, 23, 308).—It is shown that at the critical solution-temperature of two liquids many properties of the solutions follow very simple rules.

It has already been shown (*loc. cit.*) that the internal energy E of mixtures of phenol and water at their critical solution-temperature can be represented as the sum of two factors, thus $E = E_w + nE_{Ph}$, where E_w represents the internal energy of 1 mol. of water, E_{Ph} that of 1 mol. of dissolved phenol, and n the number of mols. of phenol for 1 mol. of water. It is now shown that the same rule holds for mixtures of acetylacetone and water, propionitrile and water, and resorcinol and benzene, but not for propionitrile and an aqueous solution of sodium chloride.

Further, the respective capillary coefficients ($=rsH$, where the symbols have the usual significance) of mixtures of phenol and water and of acetylacetone and water are constants independent of the composition of the solutions at the respective critical solution-temperatures. Similarly, the vapour pressure of certain pairs of liquids with an upper critical solution-temperature is independent of the composition within the limits of 20—80% at the temperature in question, and the vapour pressure of mixtures of nicotine and water is constant between 17 and 82% nicotine at the lower critical solution-temperature. At the upper critical solution-temperature, the vapour pressure of the solutions is generally greater than that of the more volatile component. Finally, the expansion-coefficient of mixtures of acetylacetone and water is approximately constant between 15 and 79% of the former component in the neighbourhood of the critical solution-temperature.

The influence of a number of compounds (acids, salts, and sugars) on the critical solution-temperature of a mixture of propionitrile and water has been determined, but there is no apparent connexion between the magnitude of the elevation and the nature of the third substance.

G. S.

An Example of Solubility Influence. WALTER HERZ (*Zeitsch. anorg. Chem.*, 1910, 65, 341—344).—The solubility of succinic acid in water at 25° is 6.72 millimols. in 10 c.c. This value is much lowered by the addition of alkali salts, the lowering being approximately proportional to the concentration of the salt in the case of potassium chloride, bromide, and iodide, but being greatest in small concentrations for sodium and lithium chlorides.

The reciprocal lowering of the solubility of sodium chloride by succinic acid has also been measured. The formula given by Rothmund and Wilsmore (*Abstr.*, 1902, ii, 447) is not exactly confirmed, owing to the high concentration of the solution.

In the salts examined, the influence increases with diminishing

electro-affinity of the metal, and also, although to a less extent, with increasing electro-affinity of the anion.

C. H. D.

Difference in the Speed of Dissolution of Sucrose Crystals at their Different Faces. GASTON GAILLARD (*Compt. rend.*, 1910, 150, 217—219).—Observations have been made on sucrose by immersing different faces of a crystal in water for a definite time. The area of the crystal face was measured, and the amount of dissolved solid determined polarimetrically. Results are given in tabular form, from which it appears that the speed of dissolution varies somewhat according to the face of the crystal undergoing attack by the solvent.

W. O. W.

Crystallisation in Fused Masses, owing to the Liberation of Gas. FRITZ RINNE (*Jahrb. Min.*, 1903, ii, 129—139).—By the evolution of a gaseous product, the composition of a fused mass may be so altered that crystallisation takes place without any fall in temperature. The conditions of equilibrium in such systems are illustrated by diagrams, and the example most fully worked out is the conversion of white cast-iron into wrought-iron by the puddling process. Samples of iron were taken at different stages of the process, the percentage of carbon determined, and sections of the metal examined under the microscope. As the carbon is burnt off, there is a crystallisation of martensite from the fluid metal. In the same way, crystallisation of silver or gold may take place during the cupellation of silver-lead or gold-lead alloys, owing to the distillation or oxidation of the lead. In aqueous solutions of salts, a similar change in composition is effected by the evaporation of the solvent; and in igneous magmas it is possible that crystallisation may also be induced by an alteration in composition accompanying the liberation of volcanic gases.

L. J. S.

Spontaneous Crystallisation of Sugar. G. FOUQUET (*Compt. rend.*, 1910, 150, 280—282).—Observations have been made on the temperature at which spontaneous crystallisation begins in super-saturated sugar solutions submitted to mechanical stirring. As a result, the author confirms the observations of Miers in the case of other substances, that the curve of supersaturation obtained by plotting concentration against the temperature at which crystallisation commences is approximately parallel to the curve of solubility. The addition of impurities does not appear to affect this parallelism.

W. O. W.

Liquid Crystals and Avogadro's Hypothesis. OTTO LEHMANN (*Zeitsch. physikal. Chem.*, 1910, 71, 355—381).—The paper consists largely of references to the author's earlier work on liquid crystals.

The generally accepted view as to the nature of liquid crystals is incompatible with Avogadro's hypothesis, and the author, therefore, considers that the hypothesis in question is not valid. The consequences drawn from it as to the identity of molecular weight in different states of aggregation (including van der Waals' theory of

continuity) cannot be upheld. The existence of a transition temperature for enantiotropic modifications, and of mixed crystals of non-isomorphous modifications, are also regarded as incompatible with Avogadro's hypothesis. The assumption made in deducing Avogadro's hypothesis from the principles of the kinetic theory, that the mass of a molecule is constant, is not applicable to gases and liquids where the molecules can readily combine and decompose.

The views as to the nature of liquid crystals advocated in different editions of Nernst's *Theoretische Chemie* are adversely criticised, and the author contends that his priority in reference to a number of discoveries referring more particularly to crystals has been disregarded by Nernst.

G. S.

Self-purification of Liquid Crystals. OTTO LEHMANN (*Physikal. Zeitsch.*, 1910, 11, 44—49).—Experiments are described which indicate that the formation of liquid crystals from isotropic liquids is accompanied by a purification process analogous to that which attends the separation of solid, crystalline aggregates from isotropic liquids. This can be observed, for instance, when very finely divided and specifically light substances (such as spores of *Lycopodium*) are added to *p*-azoxyanisole in the isotropic condition, and the temperature is then allowed to fall, so that the anisotropic form of the substance makes its appearance. The observations indicate that, in general, colloidal solutions in crystalline liquids are not obtainable. This is regarded as another argument in favour of the author's theory of the nature of liquid crystals, as against the emulsion theory. H. M. D.

Emulsions. WA. OSTWALD (*Zeitsch. Chem. Ind. Kolloide*, 1910, 6, 103—109).—In connexion with the technical impregnation of wood with coal-tar oils, the author has investigated the nature of the emulsions which are formed by oils with water. Since both the oil and the water can take the part of the disperse colloid, or of the dispersive medium, it is evident that there are two critical points which determine the limiting concentrations for disperse systems in which the respective substances play the part of disperse medium. For mixtures of the two substances which fall between these limits, two kinds of emulsions can be obtained which have quite different properties. The character of the emulsion which is formed in any given case is shown to depend on the previous history of the substances. If the carefully cleaned interior surface of the vessel in which the emulsion is prepared has been previously covered with oil, the emulsion obtained is of the one type; if previously covered with water, the second type of emulsion is obtained. The effect of a surface layer of oil is apparently to destroy the colloidal disperse oil particles which may be formed on agitation, and, similarly, the effect of a water surface is to nullify the tendency of the water to distribute itself in the form of a disperse colloidal suspended phase. H. M. D.

Independent Components and Compounds. RUDOLF RECH (*Zeitsch. physikal. Chem.*, 1910, 71, 337—354).—A theoretical paper. The conditions are investigated under which, in a two-phase system,

a system made up of n elements behaves as a system of $n - 1$ substances. For a system made up of two elements, these conditions can only be fulfilled in one way, and the simple relation $r_1/s_1 = r_2/s_2$ holds (r_1 and r_2 being the amounts of heat taken up by the system, and s_1 resp. s_2 the changes of volume which occur when unit mass of the first of the second component respectively is transferred at constant temperature and pressure from the first to the second phase), which is equivalent to the law of constant proportions for a binary compound which boils, fuses, or undergoes transition without decomposition. When n exceeds 2, the conditions may be fulfilled in different ways, but the preferable solution leads to an equation of the same form as the above, which therefore applies to a binary system on addition of other elements provided that the compound behaves to these as a whole. G. S.

Allotropy and Internal Equilibrium. ANDREAS SMITS (*Chem. Weekblad*, 1910, 7, 79—83).—A theoretical paper. A. J. W.

The Equilibrium Solid-Liquid-Gas in Binary Systems which Present Mixed Crystals. HUGO R. KRUYT (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 537—545).—A theoretical paper in which the author discusses the various possible forms of the three-phase equilibrium curves for binary systems in which the two components are completely miscible in the solid state. H. M. D.

Equilibria in Quaternary Systems. The System: Lithium Sulphate-Ammonium Sulphate-Ferrous Sulphate and Water. FRANS A. H. SCHREINEMAKERS (*Zeitsch. physikal. Chem.*, 1910, 71, 109—116).—The three ternary systems and the quaternary system have been investigated by solubility measurements at 30° in the usual way, and the results are represented in two ways on projected space diagrams.

The solid phases in the quaternary system are $(\text{NH}_4)_2\text{SO}_4$, $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Li}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 = D_{\text{Li}}$, and $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O} = D_{\text{Fe}}$.

The results show that $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ can co-exist with $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and D_{Fe} , but not with $(\text{NH}_4)_2\text{SO}_4$ and D_{Li} ; that $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ can co-exist with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, D_{Fe} , and D_{Li} , but not with $(\text{NH}_4)_2\text{SO}_4$; that $(\text{NH}_4)_2\text{SO}_4$ can co-exist with D_{Fe} and D_{Li} , but not with the other two salts; that D_{Li} can co-exist with all the other salts except $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and, finally, that D_{Fe} can co-exist with all the other solid salts. G. S.

Criteria for the Determination of the Sensitiveness of Precipitation Reactions. WILHELM BÖTTGER (*Festschrift Otto Wallach*, 1909, 282—300).—Experiments have been made to determine the smallest concentration at which potassium chloride, bromide, and iodate can be detected by the formation of a visible precipitate on the addition of silver nitrate. For this purpose, a definite volume of a solution containing a relatively large excess of silver nitrate was added to measured volumes of solutions of the halogen salts of gradually decreasing concentration. The observations indicate that the limiting concentrations for the chloride, bromide, and iodate are respectively 0.16×10^{-5} , 0.04×10^{-5} , and 1×10^{-5} mol. per litre. In the case of the

precipitation of silver chloride, the limiting concentration falls to 0.04×10^{-5} mol. per litre in presence of nitric acid. This increase in sensitiveness is attributed to the formation of particles of larger size when nitric acid is present in the solution. On the other hand, there appears to be a limit to the increase in sensitiveness on this account, for the silver iodate is precipitated in the form of well-defined, crystalline particles of relatively large size, and it is to this circumstance that the relative insensitiveness of the visible reaction between iodate and silver nitrate appears to be due.

It is shown that observations of the above nature can be utilised to determine approximately the solubility of slightly soluble substances, provided that these are not especially characterised by the ready formation of supersaturated solutions.
H. M. D.

Relationship between the Structure of the Aliphatic Alcohols and their Rate of Esterification. ARTHUR MICHAEL (*Ber.*, 1910, 43, 464—465. Compare Michael and Wolgast, *Abstr.*, 1909, ii, 873).—Polemical in reply to B. N. Menshutkin (*ibid.*, 988). It is pointed out that the methods used by N. Menshutkin and by Michael and Wolgast are essentially different, and the results are not comparable.
J. J. S.

Modification of Dunstan and Short's Extraction Apparatus. P. È. F. PERRÈDES (*Pharm. J.*, 1910, [iv], 30, 106).—In using this apparatus in its original form, the contents of the inner tube are liable to be carried into the outer tube of the extractor if the solvent is boiled vigorously. To avoid this, the author inserts a spiral spring of brass wire, provided with a suitable disk of wire gauze at the lower end, and a ring at the other. The lower end rests on the contents of the inner tube, and the other end against the cork with which the extractor is closed. The modified apparatus is figured in the original.
T. A. H.

[Lecture] **Experiments in Physical Chemistry.** UGO GRASSI (*Nuovo Cim.*, 1909; [v], 18, ii, 408—412).—The author describes suitable apparatus for (1) measuring the catalytic action of hydrochloric acid on the reaction between menthone (or acetophenone) and phenylhydrazine; (2) studying the law of mass action in the dissociation of nitrogen peroxide, and (3) measuring the lowering of solubility in water effected by a substance dissolved in ether.
T. H. P.

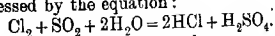
Inorganic Chemistry.

Formulation and Nomenclature of Inorganic Compounds. MAX K. HOFFMANN (*Chem. Zeit.*, 1910, 34, 73—76).—A scheme is put forward for the systematic formulation and nomenclature of inorganic compounds. The following points are considered: (1) The sequence

of the elements and radicles in the various compounds. (2) The order in which the various oxidation stages of the same element should be placed in a formula. (3) The naming of numbers, for example, mono-, di-, tri-, etc. (4) The nomenclature of (a) individual elements, (b) anions, (c) alloys, (d) metalamines, (e) double salts. (5) Method of denoting the number of components in compound (double, triple, etc.) salts. (6) Nomenclature of (a) salts of condensed acids, (b) special groups of elements. (7) Method of writing long names. (8) Use of old names. (9) Method of denoting water of crystallisation. T. S. P.

Chemical and Biological Effects of Ultra-violet Light. MAURICE LOMBARD (*Compt. rend.*, 1910, 150, 227—229. Compare Courmont, *Abstr.*, 1909, ii, 753; Aubel, this vol., ii, 28).—Owing to the contradictory results obtained by previous observers, the author has re-examined the chemical effects of quartz-mercury lamps on water. The sterilising action of the Kromayer lamp has been ascribed to the formation of hydrogen peroxide; it has been found, however, that the production of iodine from potassium iodide is more marked with a feebly alkaline, natural water than when the water is slightly acidified. Distilled water gave comparable results only after addition of a nitrate. The liberation of iodine, therefore, appears to be due to the formation of nitrites, and this has been confirmed by the production of a coloration with sulphanilic acid and α -naphthylamine. Hydrogen peroxide is probably formed first, in accordance with the equation: $2\text{H}_2\text{O} = \text{H}_2\text{O}_2 + \text{H}_2$, and this is followed by reduction of the nitrate. The sterilising action of the lamps is considered to depend on the direct action of the rays on bacteria. W. O. W.

Utilisation of Electrolytic Chlorine for the Simultaneous Production of Hydrochloric and Sulphuric Acids. ANGELO COPPADORO (*Gazzetta*, 1909, 39, ii, 616—642).—The author discusses the various processes devised for utilising the chlorine yielded by the electrolytic soda industry, and describes his own investigations on the reaction expressed by the equation:



Study of the equilibrium between the three components, water and sulphuric and hydrochloric acids, in the liquid phase at 17°, 40°, and 70° shows that, with increasing proportions of sulphuric acid, the solubility of the hydrochloric acid undergoes considerable diminution. The amount of such diminution cannot, however, be calculated by means of the formulæ given by Nerst (*Abstr.*, 1890, 3) and Noyes (*Abstr.*, 1891, 142), such formulæ giving accurate results only for dilute solutions. With Bodländer's formula (*Abstr.*, 1891, 794, 795), $W/\sqrt[3]{S} = \text{const.}$, where W and S indicate grams of water and hydrochloric acid respectively, the value of the expression is constant only for solutions containing small proportions of sulphuric acid, and increases with the amount of the latter. If, however, allowance is made for the formation of the hydrate $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ in solutions containing much sulphuric acid, the value of W being diminished by the amount of water in this hydrate, approximately constant results are obtained for the expression $W'/\sqrt[3]{S}$.

The industrial application of this process and its economics are discussed.
T. H. P.

Solubility of Gases in Concentrated Sulphuric Acid and in Mixtures of Sulphuric Acid and Water. CHRISTIAN BOHR (*Zeitsch. physikal. Chem.*, 1910, 71, 47—50).—The solubility of nitrogen, oxygen, and carbon dioxide in 96% sulphuric acid, and of the first two gases in mixtures of sulphuric acid and water in varying proportions, has been measured in the neighbourhood of 21°. The results for the 96% acid, in terms of Bunsen's absorption-coefficient $\times 100$, are as follows: carbon dioxide, 92.6; oxygen, 2.748; nitrogen, 1.292, from which it will be seen that the solubilities are not very different from those in water. The solubilities are, however, much less in mixtures of sulphuric acid and water, and for oxygen and nitrogen reach a minimum in 25*N* solution, at which the solubility is less than one-third of that in water. At the same point, the contraction on mixing sulphuric acid and water attains its maximum value.
G. S.

Amides of Sulphuric Acid. FRITZ EPHRAIM and M. GUREWITSCH (*Ber.*, 1910, 43, 138—148. Compare Abstr., 1909, ii, 994).—The methods for preparing sulphamide are far from satisfactory, and the authors have consequently investigated new methods. Theoretically, dimethyl sulphate and ammonia should give rise to sulphamide and methyl alcohol, but instead of these compounds, methylamine and ammonium methyl sulphate are formed. The difficulties met with in the preparation of methyl amidosulphonate, $\text{NH}_2 \cdot \text{SO}_2 \cdot \text{OMe}$, were too great to use that compound as the starting point.

Attempts were then made to prepare the chloroamide of sulphuric acid, $\text{Cl} \cdot \text{SO}_2 \cdot \text{NH}_2$. Amidosulphonic acid, $\text{NH}_2 \cdot \text{SO}_3\text{H}$, and phosphorus pentachloride, in the proportion of 1 : 5 by weight, readily interacted at 70—90°. After filtering the olive-green liquid so obtained through glass wool, it was distilled on the water-bath under diminished pressure. Phosphoryl chloride and phosphorus trichloride passed over, leaving a viscous, dark brown liquid, which deposited white crystals (m. p. 33—34°) after a long time at 0°. The analytical results were only in approximate agreement with the formula $\text{NH}_2 \cdot \text{SO}_2 \cdot \text{Cl} + \text{PCl}_2$. The compound is very sensitive to water and water vapour, hydrogen chloride, phosphorous acid, and amidosulphonic acid being formed. Boiling sodium hydroxide does not liberate ammonia, which is only produced on prolonged heating with fuming hydrochloric acid in a sealed tube. All attempts to decompose it into its components were unsuccessful.

When thionyl chloride and amidosulphonic acid are heated together in a sealed tube at 105—110°, ammonium chlorosulphonate, $\text{Cl} \cdot \text{SO}_2 \cdot \text{NH}_4$, is formed, and is purified by washing with carbon disulphide or light petroleum, and, after drying, it forms a white mass with a yellowish tinge (m. p. about 152° in sealed tubes). It fumes in the air, and gradually deliquesces. On treatment with liquid ammonia there is a violent reaction, the product of which dissolves in the excess of ammonia. After evaporation of the solvent, the residue is

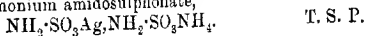
dissolved in water, the solution acidified with nitric acid, and silver nitrate added in large excess. After collecting the silver chloride, the filtrate is fractionally precipitated with ammonia, the first and smallest fraction being rejected. From a hot solution the precipitate consists of silver sulphamide, $\text{SO}_2(\text{NHAg})_2$, whereas from a cold solution it is silver imidosulphamide, $\text{NAg}(\text{SO}_2\cdot\text{NHAg})_2$, with varying amounts of water of crystallisation. Trisulphimide was not found in the reaction products.

When sulphuryl chloride is added drop by drop to liquid ammonia cooled by an ether-solid carbon dioxide freezing mixture, there is a violent reaction according to the equation: $2\text{SO}_2\text{Cl}_2 + 7\text{NH}_3 = \text{NH}(\text{SO}_2\cdot\text{NH}_2)_2 + 4\text{NH}_4\text{Cl}$. No trisulphimide is formed, and, after evaporating off the excess of ammonia, silver imidosulphamide may be obtained from the residue in a manner similar to that already described. It is always contaminated with silver sulphamide, the sulphamide being formed from the imidosulphamide according to the equation: $\text{NH}(\text{SO}_2\cdot\text{NH}_2)_2 + \text{H}_2\text{O} = \text{NH}_2\cdot\text{SO}_2\text{H} + \text{SO}_2(\text{NH}_2)_2$. In fact, silver imidosulphamide may be readily transformed into silver sulphamide by solution in dilute acid and precipitation from the warm solution by ammonia.

Pure sulphamide is best prepared by dissolving the product of the reaction between sulphuryl chloride and liquid ammonia in a small quantity of water and making the solution just acid. After two to three days the hydrolysis is complete, the mixture is evaporated to dryness in a vacuum, and the residue extracted with ethyl acetate, which dissolves out the sulphamide, amidosulphonic acid and ammonium chloride being insoluble. After evaporating off the ethyl acetate, pure sulphamide, m. p. 93° , is left.

Pure silver imidosulphamide was prepared by extracting the product of the reaction between sulphuryl chloride and liquid ammonia with ethyl acetate in order to remove the sulphamide, and then working up the residue at the ordinary temperature to silver imidosulphamide in the manner already indicated. It contained $46\text{H}_2\text{O}$.

When a solution of amidosulphonic acid is neutralised with ammonia, and the calculated quantity of silver nitrate added to form the silver salt, no precipitate forms until the liquid has been evaporated to a syrupy consistence. It then solidifies suddenly to a radiating crystalline mass, which, after crystallisation from water, gives rhombohedral crystals of silver ammonium amidosulphonate,



Allotropy of Tellurium. ERNST COHEN and J. F. KRÖNER (*Chem. Weekblad*, 1910, 7, 57—61).—A summary of the literature on the allotropy of tellurium. A. J. W.

Behaviour of Nitric Oxide at Low Temperatures. KAROL ADWENTOWSKI (*Bull. Acad. Sci. Cracow*, 1903, 742—767).—The gas investigated by the author was prepared by the action of nitric acid on ferrous sulphate or of sulphuric acid on a solution containing potassium iodide and potassium nitrite, and was purified by condensation and fractional distillation.

The relative density of nitric oxide remains unchanged when the temperature is lowered to about -150° . The mean coefficient of expansion at 760 mm. between -140° and 0° is 0.0037074. Liquid nitric oxide is colourless in thin layers, and light blue when examined in thick layers. It is, however, probable that the blue colour is due to traces of nitrogen trioxide which cannot be removed by fractionation. The critical temperature is -92.9° , the critical pressure 64.6 atmospheres. It boils at -150.2° , and solidifies at -160.6° . The vapour pressure at this temperature being 168 mm. of mercury.

The vapour-pressure curve of liquid nitric oxide is somewhat anomalous, and this is attributed to polymerisation of the molecules at low temperatures. The fact that the vapour density at atmospheric pressure is quite normal at these temperatures indicates, however, that the dissociation of the polymerised molecules is practically complete at this pressure. The high density of the liquid at its boiling point, D 1.269, is cited as evidence in support of the view that the liquid molecules are associated.

H. M. D.

Molecular Weight of Nitrous Acid in Aqueous Solution.
ALEXIS V. SAPOSHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1704—1708).—That the molecule of nitrous acid in aqueous solution is represented by the formula HNO_2 is partly confirmed by Schümann's measurements of the electrical conductivity and affinity constant of the acid (*Abstr.*, 1900, ii, 264). Simple shaking of solutions of nitrous acid with chloroform results in the expulsion of the anhydride, N_2O_3 , the appearance of which is explainable as due either to the occurrence of the anhydride in the solution or to the slight stability of the acid and its consequent decomposition into water and nitrogen trioxide under the influence of the chloroform. Cryoscopic measurements of aqueous solutions of nitrous acid give the molecular weights 46.0, 46.6, and 46.6, which are very nearly identical with the value, 47, required by the formula HNO_2 .

T. H. P.

Compounds of Sulphur and Phosphorus. V. Tetraphosphorus Trisulphide, P_4S_3 . ALFRED STOCK [with MAX RUDOLPH] (*Ber.*, 1910, 43, 150—157).—The author has shown previously that the only three compounds of phosphorus and sulphur are P_4S_3 , P_4S_7 , and P_2S_5 (P_4S_{10}) (compare *Abstr.*, 1909, ii, 569). The present communication describes the preparation and properties of the first compound, tetraphosphorus trisulphide.

An excess of red phosphorus is mixed with finely-powdered sulphur, and the mixture heated in a wide tube, sealed at one end, in an atmosphere of carbon dioxide. The temperature is first gradually raised to 100° , and then the reaction started by stronger local heating near the surface of the mixture. When the reaction has spread through the whole mass, the tube is strongly heated until the contents begin to distil, otherwise higher sulphides of phosphorus are formed; the reaction product, which consists of red phosphorus and tetraphosphorus trisulphide, is allowed to cool in the atmosphere of carbon dioxide. The trisulphide may be separated from the red phosphorus by extraction with carbon bisulphide or by distillation in an

atmosphere of carbon dioxide, but in both cases it is somewhat impure.

After purification and recrystallisation from benzene, a pure light-yellow product is obtained, which sinters at 171.5° , m. p. 172.5° .

The b. p. is $407-408^{\circ}/760$ mm., but at the same time there is slight decomposition, as indicated by a variation in the melting point. $D^{17}_4 = 2.03$. The molecular weight, both in carbon disulphide solution and as vapour, corresponds with the formula P_4S_3 . At 17° , 1 part by weight of P_4S_3 is dissolved by 1, 40, and 32 parts by weight respectively of carbon disulphide, benzene, and toluene. The concentrated solutions are intensely yellow.

Tetraphosphorus trisulphide is decomposed by both concentrated and dilute potassium hydroxide solution, hydrogen and phosphine (1:1 to 2:1) being evolved. The evolution of gas lasts for days at the ordinary temperature. If the brownish-red solution is acidified immediately after being prepared, a yellow precipitate, resembling solid phosphorus hydride, $P_{12}H_2$, is obtained, which decomposes and becomes brown after a time. This precipitate is not obtained from solutions which have been preserved for some time. T. S. P.

Compounds of Sulphur and Phosphorus. VI. Tetraphosphorus Heptasulphide, P_4S_7 . ALFRED STOCK [with BERLA HERSCOVICI] (*Ber.*, 1910, 43, 414-417).—An intimate mixture of purified red phosphorus and sulphur, in such proportions that the reaction product would consist of $P_4S_7 + 5\% P_4S_3$, is heated in a hard glass tube in the way described in the preparation of tetraphosphorus trisulphide (preceding abstract) until distillation begins. The cooled product is then recrystallised from carbon disulphide, in which the heptasulphide is sparingly soluble (1 part in 3500 parts solvent at 17° , and 1 part in 20,000 parts at 0°), whilst the trisulphide is readily soluble.

Tetraphosphorus heptasulphide crystallises in small, slightly yellow prisms, $D^{17}_4 = 2.19$, sinters at $305-308^{\circ}$, m. p. 310° .

The b. p. is $523^{\circ}/760$ mm., and the vapour density at 700° corresponds with the formula P_4S_7 ; above 750° the vapour density rapidly diminishes to one-half its normal value. At the ordinary temperature, it is stable, but on melting, and at higher temperatures, it decomposes to some extent. It is more sensitive to moisture than the trisulphide. When exposed to the air for some time, it smells strongly of hydrogen sulphide. T. S. P.

Crystalline Boron. II. HEINRICH BILTZ (*Ber.*, 1910, 43, 297-306).—So-called crystalline boron has hitherto been obtained in two different crystalline forms, the one being black and having the formula AlB_{12} , whilst the other consisted of colourless to yellow, quadratic crystals, having the composition $C_2Al_2B_{48}$ (Hampe, this Journ., 1877, i, 273). The preparation of the colourless crystals has hitherto been a very troublesome matter, but the author obtains them readily as follows: A mixture of 50 grams of boron trioxide, 75 grams of sulphur, 100 grams of aluminium, and 2 grams of soot is fired by an

appropriate tuse. The fused mass is treated with water and concentrated hydrochloric acid, and the residue finally left under dilute hydrochloric acid for some days. When all action has ceased, it is well washed by decantation with hot water. The resulting preparation consists mostly of the transparent, yellow, quadratic crystals, but it is also mixed with the black crystals. The black crystals have $D_4^{20} = 2.554 \pm 0.005$, and the yellow, $D_4^{20} = 2.590 \pm 0.006$, and are separated by the flotation method in a mixture of methylene iodide and benzene.

The quadratic crystals are not attacked by hot concentrated hydrochloric acid or sulphuric acid, or by a solution of chromium trioxide in concentrated sulphuric acid. They are dissolved by hot concentrated nitric acid, especially when heated in a sealed tube at $150-180^\circ$. In transmitted light they are yellow to brownish-yellow in colour, whereas in reflected light they are dark brown to grey. Analysis gave 4.07% C, 13.38% Al, and 82.1% B (= total of 99.6%), which corresponds with the formula $C_2Al_3B_{44}$, which is slightly different from that obtained by Hampe (*loc. cit.*). It is not possible to say whether these crystals are a definite chemical compound or a saturated mixed crystal.

T. S. P.

Action of Carbon Tetrachloride Vapour on Anhydrides and Oxides. PIERRE CAMBOULIVES (*Compt. rend.*, 1910, 150, 175-177).—The author gives in tabular form a list of those oxides which undergo conversion into chlorides or oxychlorides when heated in a stream of carbon tetrachloride vapour; the nature of the products is indicated, as well as the temperature at which the reaction commences. No action occurs with the oxides of boron and silicon. In other cases, chlorination occurs between 215° and 580° . The oxides of niobium and thorium give a mixture of oxychloride and chloride, whilst tungstic oxide gives the oxychloride only. All the other metallic oxides examined yielded the corresponding chloride.

W. O. W.

Action of Carbon Tetrachloride Vapour on Minerals. PIERRE CAMBOULIVES (*Compt. rend.*, 1910, 150, 221-223. Compare preceding abstract).—The ease with which natural or artificial metallic oxides undergo chlorination when heated in carbon tetrachloride vapour renders possible the application of this substance to the analysis of complex minerals. A separation of free and combined silica in bauxite, for example, can be effected in this way, since aluminium silicate is transformed into the chlorides of aluminium and silicon, whilst uncombined silica is not attacked. In the same manner, molybdenite has been shown to contain free molybdenum oxide.

W. O. W.

Conductivity of the Inner Cone of Divided Flames. The Explosibility of Gaseous Mixtures. FRIEDRICH EPSTEIN and P. KRASSA (*Zeitsch. physikal. Chem.*, 1910, 71, 28-46).—The authors describe the experimental work on which the conclusions of Haber (this vol., ii, 122) as to the connexion between luminosity and electrical conductivity in the Bunsen flame are partly based.

A steady flame was secured by thorough mixing of the coal-gas and

air before reaching the burner. As electrodes for the conductivity measurements, two platinum-iridium wires 0.05 mm. in diameter were stretched horizontally across the flame; they were fixed 1—2 mm. apart, and the position of the cone of the flame with reference to them could be altered by means of a screw arrangement. In order to minimise the effect of the ends of the electrodes, and thus obtain more regular results, 3 cm. in the middle of each wire was covered with magnesium oxide. Measurements of temperature were made simultaneously by means of a thermo-couple.

As the electrodes are gradually lowered in the flame, the electrical conductivity increases regularly, but there is a sudden increase when the electrodes reach the luminous cone. In one experiment with the electrodes 1 mm. apart, the conductivity was three to four times greater at the summit of the luminous zone than at a point 1 mm. above it. As the proportion of oxygen in the mixture is gradually diminished, the change of conductivity on reaching the luminous zone is less abrupt, a result which is due in part to the lowering of temperature. The addition of carbon dioxide to the gas mixture also renders the change of conductivity at the margin of the luminous zone less sharp, but at the same time broadens out the luminous zone, so that in this case, also, there is a close connexion between conductivity and luminosity. Further, in the case of the carbon monoxide flame, which is only slightly luminous, there is no great increase of conductivity on reaching the inner cone.

Contrary to the general opinion as to the action of an inert gas on the luminosity of a flame, it was found that when the supply of gas and air was kept constant, and carbon dioxide was added to a flame; it became more explosive, and it is even possible in this way to bring about the separation of an undivided flame. This conclusion is borne out by the results of Eitner (*Habilitationsschrift*, München, 1902), which are discussed at length. In this connexion, it is shown that Le Chatelier's rule, according to which the lower limit of explosibility of a gaseous mixture is an additive function of its composition, is approximately valid, but this rule does not hold for the higher limit of explosibility.

G. S.

Existence of Real Percarbonates and their Differentiation from Carbonates with Hydrogen Peroxide of Crystallisation. SEBASTIAN TANATAR, *Ber.*, 1910, 43, 127—128).—Riesenfeld and Reinhold (this vol., ii, 33) class the potassium percarbonate of Constam and Hansen as a real percarbonate, because it liberates iodine immediately from neutral potassium iodide, whereas Tanatar's sodium percarbonate does not react in this way, and is therefore considered to be a carbonate with hydrogen peroxide of crystallisation.

The author points out that these reactions prove nothing, and could be foreseen. Potassium percarbonate ($K_2C_2O_6$) forms potassium hydrogen carbonate in aqueous solution, and this would have no action on iodine, whereas not hydrogen carbonate, but carbonate is contained in aqueous solutions of Tanatar's sodium percarbonate. The carbonate would prevent the liberation of iodine owing to the formation of hypiodite; the latter compound would then react with hydrogen

peroxide with evolution of oxygen, as observed by Riesenfeld and Reinhold.

The author states that he does not bind himself to any particular conception of the constitution of his percarbonates.

T. S. P.

So-called Amorphous Silicon. ERNST WILKE-DÜRENFURT (*Festschrift Otto Wallach*, 1909, 671—684).—The form of silicon which is obtained in the reduction of silicon fluoride by sodium at a dull red heat reacts readily with sulphuric acid and with hot water. In the former case, sulphur is formed as one of the reduction products. The great readiness with which the silicon reacts on these substances explains the poor yields which have been obtained by previous workers who have prepared amorphous silicon by this process. It also prevents this process from being economically used for the preparation of large quantities of the reactive amorphous form.

A similar amorphous product is obtained with a comparatively high yield when sodium silicofluoride is melted together with sodium and aluminium, and the metallic regulus obtained is treated with acids. This first product, of a grey colour, is not very reactive, and on that account it can be separated more or less completely from admixed silica. When heated with hydrofluoric acid, the greyish-coloured variety of silicon is, however, converted into a brown variety, which is very much more reactive. The product thus obtained is violently attacked by concentrated nitric acid, with the formation of a white substance which appears to be a nitride, since it evolves ammonia when acted on by sodium hydroxide. When heated, the brown, amorphous silicon is transformed into a much less active form.

Many apparently conflicting statements in the literature can be explained on the basis of the author's observations.

H. M. D.

Alloys of the Chlorides of the Alkali Metals. S. F. SCHEMITSCHUSCHNY and F. RAMBACH (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1785—1814. Compare Kurnakoff and Schemitschuschny, *Abstr.*, 1906, ii, 443).—The authors have traced the melting-point and solidification curves of binary mixtures of the chlorides of the alkali metals.

For lithium and potassium chlorides, the m. p. diagram consists of two branches meeting at the eutectic point 352° , which corresponds with 40.5 mol. % KCl and 59.5 mol. % LiCl. Solid solutions are not formed, the two components separating from the molten mixtures in the pure state. The molecular depression of the m. p. of lithium chloride (100 mols.) by potassium chloride is $4.5-4.3^{\circ}$, whilst with potassium chloride as solvent, the molecular depression is $4.9-4.8^{\circ}$. The eutectic alloy, m. p. 352° , furnishes a good protecting layer for metals which oxidise on heating to $400-500^{\circ}$. The m. p. of lithium chloride is 614° (Carnelley, this Journ., 1876, i, 489, found $602 \pm 5^{\circ}$; and Guntz, *Zeitsch. angew. Chem.*, 1898, 11, 158—159, 600°).

With lithium and rubidium chlorides, the curve is composed of two branches, which meet at the eutectic point 312° , corresponding with 44.75 mol. % RbCl and 55.25 mol. % LiCl; no solid solutions are formed. The molecular depression for lithium chloride is $4.3-4.1^{\circ}$.

and for rubidium chloride, $4.6-4.3^{\circ}$. Rubidium chloride has m. p. 726° (Carnelley, *Trans.*, 1878, 33, 273, found 710°).

For lithium and sodium chlorides the cooling curves exhibit no eutectic halt, solidification proceeding over a certain interval of temperature, and solid solutions of various concentrations being formed. The m. p. diagram is a continuous curve of Roozeboom's type III, exhibiting a minimum at 352° , corresponding with 27 mol. % NaCl. The molecular depression of the m. p. of sodium chloride is $3.8-3.7^{\circ}$, and of the lithium salt, 2.5° .

With rubidium and potassium chlorides the m. p. curve is continuous, and proceeds at first almost horizontally and then gradually rises to the m. p. of potassium chloride. Solid solutions are formed in all proportions of the components, the m. p. curve being of Roozeboom's type I. These observations are confirmed by the structures of the alloys. The molecular depression of rubidium chloride is in this case negative and equal to $0.15-0.11^{\circ}$, whilst for the potassium salt it amounts to $1.4-1.3^{\circ}$.

The m. p. diagram of rubidium and sodium chlorides consists of two branches meeting at the eutectic point 541° , which corresponds with 54.96 mol. % RbCl. The molecular depression is $4.4-4.0^{\circ}$ for rubidium chloride, and $4.3-4.1^{\circ}$ for sodium chloride.

Cesium chloride has m. p. 646° (Carnelley and Williams, *Trans.*, 1880, 37, 125, gave 631°). The cooling curves for mixtures of rubidium and cesium chlorides exhibit two halts, the second, at 451° , being conditioned by the existence of a polymorphous modification of cesium chloride. The ratio of the heat of transformation into this second modification to the latent heat of fusion of cesium chloride is found to be 0.35. The m. p. diagram is a continuous curve of Roozeboom's type III, and exhibits a minimum at 440° , corresponding with 11.5 mol. % of rubidium chloride. The molecular depression for cesium chloride is $1.6-1.5^{\circ}$, and for rubidium chloride, $1.6-1.5^{\circ}$.

With cesium and potassium chlorides, the m. p. diagram is a continuous curve (Roozeboom's type III) with a minimum at 616° , corresponding with 34 mols. % KCl. None of the cooling curves show a eutectic halt, solid solutions of various concentrations being formed. The presence of potassium chloride lowers the temperature of polymorphous transformation of cesium chloride; with 11.5 mol. % of KCl, the change becomes very indistinct, and with higher proportions disappears completely. The molecular depression is 1.1° for cesium chloride and $2.8-2.9^{\circ}$ for potassium chloride.

For sodium and cesium chlorides the m. p. diagram is formed of two branches meeting at 493° , which corresponds with 34.5 mol. % NaCl; no solid solutions are formed. Similar results are obtained with the system $\text{CsCl} + \text{LiCl}$.

These chlorides may be divided into two groups: (1) those of potassium, rubidium, and cesium, which mix in all proportions, and (2) those of lithium and sodium, which at high temperatures form uninterrupted series of solid solutions, these decomposing at lower temperatures.

By means of van't Hoff's formula, the latent heats of fusion are

found to be: for NaCl, 97; LiCl, 86; KCl, 63; RbCl, 38, and CsCl, 24 Cals., these values diminishing with increase of the molecular weight.

The heats of formation of a number of the solid solutions formed by the above salts have been measured, and it is found that, in all cases, considerable absorption of heat occurs, the solid solutions being consequently unstable and undergoing gradual decomposition.

T. II. P.

Some Thiophosphates. FRITZ EPHRAIM and ETTA MAJLER (*Ber.*, 1910, 43, 285—288).—When solid sodium tetrathiosulphate, Na_4PS_4 (compare Abstr., 1905, ii, 318), is treated with the solutions of sulphides of other metals, reaction takes place either according to the equation $2\text{Na}_4\text{PS}_4 + 3\text{M}_2\text{S} + 2\text{H}_2\text{O} = 2\text{M}_3\text{PS}_3\text{O} + 3\text{Na}_2\text{S} + 2\text{H}_2\text{S}$, or according to the equation: $2\text{Na}_4\text{PS}_4 + 3\text{M}_2\text{S} + 4\text{H}_2\text{O} = 2\text{M}_3\text{PS}_3\text{O}_2 + 3\text{Na}_2\text{S} + 4\text{H}_2\text{S}$. In no case is the tetrathiosulphate of the second metal formed, owing to hydrolysis by the water.

Barium oxytrithiophosphate, $\text{Ba}_3(\text{PS}_3\text{O})_2 \cdot 20\text{H}_2\text{O}$, was obtained from sodium tetrathiosulphate and a solution of barium sulphide. It is stable when dry, but is decomposed by water or dilute acids with evolution of hydrogen sulphide. Concentrated nitric acid dissolves it, the sulphur being completely oxidised to sulphuric acid. When barium hydrosulphide is used instead of the sulphide, **barium dioxodithiophosphate**, $\text{Ba}_3(\text{PS}_2\text{O}_2)_2 \cdot 18\text{H}_2\text{O}$, is obtained (compare Stock, Abstr., 1906, ii, 535). Attempts to prepare strontium and calcium thiophosphates were unsuccessful.

Magnesium oxytrithiophosphate, $\text{Mg}_3(\text{PS}_3\text{O})_2 \cdot 20\text{H}_2\text{O}$, was obtained from magnesium hydrosulphide: It was precipitated from solution by alcohol in the form of white needles. It is decomposed by water or dilute acids.

T. S. P.

Selenophosphates. FRITZ EPHRAIM and ETTA MAJLER (*Ber.*, 1910, 43, 277—285).—Selenophosphates of the alkali and alkaline-earth metals and of magnesium can be prepared by the action of phosphorus pentaselenide on aqueous solutions of the selenides of the respective metals, the reaction proceeding according to the equation: $3\text{M}_2\text{Se} + \text{P}_2\text{Se}_5 = 2\text{M}_3\text{PSe}_4$. In no case, however, could a solid tetraselenophosphate be obtained, water decomposing it thus: $\text{M}_3\text{PSe}_4 + \text{H}_2\text{O} = \text{M}_3\text{PSe}_3\text{O} + \text{H}_2\text{Se}$. In some cases the decomposition may go further still, with the formation of the compound $\text{M}_3\text{PSe}_2\text{O}_2$, or even M_3PSeO_2 . In many cases intermediate compounds, for example, $\text{K}_3\text{PSe}_3\text{O}_{1.5}$, are formed, which the authors consider may be isomorphous mixtures of the different oxy-selenophosphates. If the compounds crystallise from a mother liquor rich in hydrogen selenide, they are also rich in selenium, but if precipitated by alcohol they are poorer in selenium.

The oxy-selenophosphates may also be prepared from the hydroxide of the metal and phosphorus pentaselenide. Even in the presence of excess of alkali, the normal salts sometimes hydrolyse with the formation of the monohydrogen salts, the process being conditioned by the relative solubilities of the two salts in the mother liquor.

On solution in water, especially in hot water, all the compounds decompose according to the equation: $\text{M}_3\text{PSe}_4 + 4\text{H}_2\text{O} = \text{M}_3\text{PO}_4 +$

4H₂Se. The mother liquors oxidise quickly on exposure to the air, becoming red and depositing selenium. The solid salts are fairly stable in dry air.

Normal salts were only obtained with the alkali metals; the alkaline-earth metals give monohydrate salts.

An ammonium tellurophosphate could not be obtained.

Sodium trioxyselenophosphate, Na₃PSeO₃·20H₂O, was prepared by digesting a strong solution of sodium hydroxide with phosphorus pentaselenide. The same substance was obtained when sodium hydroselenide was used in the place of sodium hydroxide. It crystallises in needles.

Ammonium oxytriselenophosphate was obtained from phosphorus pentaselenide and a saturated solution of hydrogen selenide in strong ammonia. From the warm mother liquor, leaflets crystallised having the composition (NH₄)₃PSe₃O₃·10H₂O, and later the cold mother liquor deposited octahedra and four-sided leaflets of the composition (NH₄)₃H(PSe₃O₃)·18H₂O.

Potassium oxyselenophosphate, K₃PSe₃O₃·5H₂O, was obtained in the form of greenish-yellow octahedra by using potassium hydroselenide. It reacts violently with nitric acid.

Barium dioxyselenophosphate, BaH₂PSe₂O₃·14H₂O, is formed when phosphorus pentaselenide is treated either with a solution of barium hydroxide, or with a saturated solution of hydrogen selenide in barium hydroxide. It forms a white, micro-crystalline powder.

When 2 grams of strontium hydroxide, dissolved in a little water, were treated with 3 grams of phosphorus pentaselenide and the filtrate from the deposited selenium treated with alcohol, a light yellow precipitate of a *strontium oxyselenophosphate*, having the composition SrH₂PSe₂O₃·7H₂O, was obtained. When a larger excess of the pentaselenide was used, the crystals were colourless, and had the composition SrH₂PSe₂O₃·8H₂O, which may possibly be 2SrH₂PSeO₃·SrH₂PSe₂O₃·24H₂O.

With calcium hydroxide a *calcium oxyselenophosphate* was formed. With the smaller proportion of phosphorus pentaselenide, the yellow crystals obtained had the composition CaH₂PSe₂O₃·5H₂O, whilst with the larger proportion their composition was CaH₂PSe₂O₃·8H₂O.

A *magnesium dioxyselenophosphate* was also obtained, but not in a pure condition.

T. S. P.

Lithium Phosphomolybdates. FRITZ EPHRAIM and MAX BRAND (*Zeitsch. anorg. Chem.*, 1910, 65, 233–236).—Five lithium phosphomolybdates, two of which are of rather complicated composition, have been prepared.

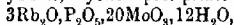
The salt, 3Li₂O·P₂O₅·5MoO₃, with both 16H₂O and 17H₂O, is obtained from the mother liquor of its additive compound, described below, in white prisms. The salt, 5Li₂O·2P₂O₅·8MoO₃·28H₂O, is obtained when lithium carbonate, phosphoric acid, and molybdenum trioxide are mixed in the proportions of the first salt, and the solution is evaporated. It forms long, slender needles, readily soluble in water. The salt, 3Li₂O·P₂O₅·12MoO₃·18H₂O, is obtained on adding dilute nitric acid to the first salt in concentrated solution, and forms a yellow,

micro-crystalline precipitate. When the mother liquor is evaporated, orange crystals of the salt, $3\text{Li}_2\text{O}, \text{P}_2\text{O}_5, 18\text{MoO}_3, 27\text{H}_2\text{O}$, are obtained.

The double salt, $3\text{Li}_2\text{O}, \text{P}_2\text{O}_5, 6\text{MoO}_3 + 6\text{Li}_3\text{PO}_4, 18\text{H}_2\text{O}$, is obtained when 52 grams of lithium molybdate are dissolved, and 29 grams of molybdenum trioxide and 15 grams of phosphoric oxide added. It crystallises in short rods, and has an alkaline reaction, whilst the other lithium phosphomolybdates are acid. Water decomposes it, leaving a residue of lithium phosphate.

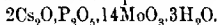
C. H. D.

Rubidium and Cæsium Phospho- and Arseni-molybdates. FRITZ EPHRAIM and HEINRICH HERSCHFINKEL (*Zeitsch. anorg. Chem.*, 1910, 65, 237—247).—The salt, $7\text{Rb}_2\text{O}, \text{P}_2\text{O}_5, 22\text{MoO}_3, 12\text{H}_2\text{O}$, is obtained by mixing the components in the molecular proportions 3 : 1 : 2, when a yellow salt, usually slightly green owing to partial reduction, is precipitated. By the addition of nitric acid, D 1·2, to a solution of rubidium phosphomolybdate, a yellow precipitate of the salt,



is obtained. If this salt is suspended in water, and rubidium carbonate is added until the yellow colour of the solid disappears, a white salt, $6\text{Rb}_2\text{O}, \text{P}_2\text{O}_5, 18\text{MoO}_3, 10\text{H}_2\text{O}$, is obtained. If 0·5 mol. phosphoric acid is added to 1 mol. rubidium carbonate, and then boiled with 1 mol. molybdenum trioxide, a solution is formed which deposits very large crystals of the salt, $5\text{Rb}_2\text{O}, 2\text{P}_2\text{O}_5, 9\text{MoO}_3, 13\text{H}_2\text{O}$. The last portions of the mother liquor deposit crystals of $7\text{Rb}_2\text{O}, 3\text{P}_2\text{O}_5, 10\text{MoO}_3, 15\text{H}_2\text{O}$.

A yellow cæsium salt has the composition



A white salt, $3\text{Cs}_2\text{O}, \text{P}_2\text{O}_5, 6\text{MoO}_3, 8\text{H}_2\text{O}$, is obtained similarly to the white rubidium salt.

A simple rubidium arsenomolybdate, $\text{Rb}_2\text{O}, \text{As}_2\text{O}_5, 6\text{MoO}_3$, is obtained as a white, micro-crystalline precipitate by adding rubidium nitrate to a concentrated solution of arsenomolybdic acid (Pufahl, Abstr., 1884, 715). A salt, $4\text{Rb}_2\text{O}, \text{As}_2\text{O}_5, 18\text{MoO}_3, 40\text{H}_2\text{O}$, is obtained as a yellow precipitate by mixing molecular proportions of rubidium hydroxide and molybdenum trioxide, and then adding nitric acid and arsenic acid. If an excess of arsenic acid is used, colourless crystals of the salt, $3\text{Rb}_2\text{O}, 3\text{As}_2\text{O}_5, 5\text{MoO}_3, 9\text{H}_2\text{O}$, are obtained, readily soluble in water. It contains more arsenic than any previously known arsenomolybdate.

A yellow cæsium arsenomolybdate, $4\text{Cs}_2\text{O}, \text{As}_2\text{O}_5, 26\text{MoO}_3, 15\text{H}_2\text{O}$, is obtained in similar manner. It was not found possible to prepare a white cæsium salt, the product isolated being cæsium arsenate, $\text{Cs}_2\text{O}, 2\text{As}_2\text{O}_5, 5\text{H}_2\text{O}$, which forms well-developed crystals. C. H. D.

Dimorphism of Ammonium Haloids. ROBERT C. WALLACE (*Centr. Min.*, 1910, 33—36).—When ammonium chloride is sublimed there is a marked change in the heat effect at 159° ; under the microscope the crystals exhibit a change at this temperature, although they still remain optically isotropic; and on cooling in a dilatometer filled with oil, the crystals show an appreciable contraction in volume at this point. Ammonium bromide exhibits the same reversible phenomena at 109° , but ammonium iodide shows no change.

The molecular volumes of ammonium chloride and ammonium

bromide in their modifications stable at the ordinary temperature indicate that these (more highly polymerised) salts are not isomorphous with the potassium haloids and ammonium iodide; but it is probable that the modifications stable at the higher temperatures do belong to this isomorphous series.

L. J. S.

Properties of Precipitated Silver. TARAK NATH DAS (*Chem. News*, 1910, 101, 51).—When the solution of hypophosphite obtained in the preparation of phosphine from phosphorus and sodium hydroxide is acidified and treated with silver nitrate, a yellow precipitate of silver separates after a time, and gradually changes in colour, becoming successively brown, red, grey, and finally black. The precipitate dissolves very readily in solutions of potassium cyanide and potassium chlorate, less readily in sodium thiosulphate, and is nearly insoluble in ammonia and sodium hydroxide.

H. M. D.

Atomic Weight of Strontium. Sir EDWARD THORPE and ARTHUR G. FRANCIS (*Proc. Roy. Soc.*, 1910, A, 83, 277—289).—The atomic weight of strontium has been determined by measurement of the ratios (1) $\text{SrBr}_2 : 2\text{Ag}$ (6 determinations), (2) $\text{SrBr}_2 : 2\text{AgBr}$ (5 determinations), (3) $\text{SrCl}_2 : 2\text{Ag}$ (6 determinations), (4) $\text{SrCl}_2 : 2\text{AgCl}$ (5 determinations). The strontium salts were purified by very extensive processes of fractional crystallisation, and all reagents used in connexion with the measurements were freed from possible impurities by suitable methods. From the four ratios, the atomic weight of the metal is found to be 87.646 ± 0.0016 .

In order to obtain an independent check on these determinations, two further series were made, depending on the ratio of SrSO_4 to SrCl_2 and SrBr_2 (4 and 3 determinations) respectively. In consequence of the more complicated character of the manipulative processes involved in these estimations, the accuracy obtainable by this method is not so high as in the methods of the first four series. The mean value obtained for the atomic weight is 87.645 ± 0.0107 . As a final result, the authors adopt the number 87.65, which is only 0.03 in excess of that obtained by Richards.

H. M. D.

Action of some Salts of Ammonium on the Alkaline Earth Carbonates. ERTORE SELVATICI (*Bull. Assoc. Chim. Sucr. Dist.*, 1910, 27, 669—670).—It is proposed to prepare barium chloride and nitrate, and the corresponding strontium compounds, by heating the carbonates with equal mol. weights of ammonium chloride and nitrate respectively. The barium nitrate may be used for preparing the oxide by heating to redness in a current of oxygen, and the peroxide by merely heating to redness.

N. H. J. M.

Electrolysis of Cupric Solutions. OCTAVE DONY-HÉNAULT (*Bull. Soc. chim. Belg.*, 1910, 24, 56—83).—A reply to Foerster (*Abstr.*, 1909, ii, 314) on behalf of Meyer (*Abstr.*, 1908, ii, 803; 1909, ii, 314). As the result of new experiments, the author concludes that the explanation given by Meyer holds for temperatures below 50° , whilst that due to Foerster, Abel, and others is true for

temperatures near the boiling point. Luther's method of estimating cuprous salts by means of permanganate (Abstr., 1901, ii, 301) gives results concordant with those obtained by weighing the copper which separates when a solution of copper sulphate in dilute sulphuric acid, which has been heated at 200° in presence of copper, is cooled. For neutral solutions, the results obtained by the two methods do not agree. Luther's value for the equilibrium constant Cu/Cu_2 is confirmed. T. A. H.

Coloration of Salts. ANDRÉ RASSENFOSSE (*Bull. Acad. roy. Belg.*, 1909, 1289—1321).—The various theories which have been advanced to account for the colour changes of solutions of cupric and cobaltous salts do not give a full explanation of the subject (compare Donnan and Bassett, *Trans.*, 1902, 81, 939, and Werner, *Abstr.*, 1909, ii, 49).

In the case of copper sulphate, the colour of a solution is shown to depend (a) on the dissociation of the salt, and (b) on its hydration. Evidence is brought forward to show that in the case of cupric chloride solutions, colour changes induced by the addition of hydrochloric acid by heating, by the action of alcohol, and in other ways are probably due to the formation of compounds of cupric chloride either with the reagent used or with a product of its own decomposition. In this connexion, reference is made to the additive products of hydrochloric acid with cupric, cobaltous, mercuric, and other chlorides isolated by Engel (Abstr., 1888, 558, 918, 1042, 1248; 1890, 109, and 1892, 569).

The addition of hydrochloric acid to a cold saturated solution of cupric chloride causes the precipitation of either the mono- or di-hydrate of cupric chloride, so that the colour change caused by the addition of the acid cannot be due to dehydration of the salt. Further, addition of a dehydrating agent, such as phosphoric oxide, induces no colour change in cupric chloride solution. Zinc chloride added to a green solution of cupric chloride containing hydrochloric acid restores the blue colour, probably because the zinc chloride destroys the cupric chloride hydrochloride existing in the green solution. Sodium, potassium, or barium chloride does not react in the same way as zinc chloride, but calcium or magnesium chloride changes the blue colour of an aqueous solution of cupric chloride to green, probably by the formation of a molecular compound of the two salts. A mixture of saturated solutions of cupric and calcium chlorides deposits after a time a mass of greenish-brown, deliquescent needles of the *double salt*, $2\text{CuCl}_2 \cdot \text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. When a solution of cupric chloride in water is boiled, the colour changes to green, the water vapour evolved contains hydrogen chloride, and the boiled solution on cooling shows less absorption for light and an increased electrolytic resistance. Such a solution contains cupric oxide. The blue colour is restored to the hot solution if zinc or mercuric chloride is added. A solution of anhydrous cupric chloride in ethyl alcohol deposits on evaporation under reduced pressure greenish-yellow crystals of an *additive product*, $\text{CuCl}_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$, and a similar *product* is formed with *isobutyl* alcohol. It is probably to the existence of the former substance that

the green colour of an aqueous solution of cupric chloride to which alcohol has been added is due. Cupric chloride is decomposed by paper, and to this cause is due the brown stain produced on drying paper which has been soaked in cupric chloride solution. Similar evidence in favour of the view that colour changes in cupric chloride solution are due to the formation or decomposition of compounds of the type indicated, is afforded by comparison of the absorption spectra and electrolytic resistances of such solutions.

T. A. H.

Reactions in Non-Aqueous Solutions. V. In Ethyl Acetate.

ALEXANDER NAUMANN [with MAX HAMERS and EMIL HENNINGER] (*Ber.*, 1910, 43, 313—321. Compare *Abstr.*, 1909, ii, 1018).—The anhydrous ethyl acetate used distilled at 74.5°/750 mm., and had $D_4^{20} = 0.8995$. For the experiments, half-saturated solutions were used. A list is given of salts which are soluble or insoluble in ethyl acetate.

When hydrogen sulphide is passed into strongly ammoniacal ethyl acetate, a precipitate of ammonium hydrosulphide, in the form of white leaflets, is obtained. The colourless liquid gradually becomes yellow, owing to the formation of polysulphide. The same compound is formed when ammonia is passed into a solution of hydrogen sulphide, but it then crystallises in needles. With hydrogen chloride the ammoniacal solution of ethyl acetate gives a precipitate of ammonium chloride.

At 18° a saturated solution of mercuric chloride in ethyl acetate contains one part of solute to 2.05 parts of solvent. With hydrogen sulphide, a white compound, $\text{HgCl}_2 \cdot 2\text{HgS}$, is produced, and with ammonia the compound $\text{HgCl}_2 \cdot 2\text{NH}_3$. Hydrogen sulphide and ammonia together give a greyish-black precipitate of mercuric sulphide. Molecular-weight determinations by the boiling-point method gave 254.9—269.2 as the molecular weight of mercuric chloride when dissolved in ethyl acetate.

Mercuric bromide dissolves in ethyl acetate to the extent of one part in 7.66 at 18°. Hydrogen sulphide gives a yellow precipitate of the composition $\text{HgBr}_2 \cdot 2\text{HgS}$, and ammonia a white precipitate with the composition $\text{HgBr}_2 \cdot 2\text{NH}_3$. Ammonia and hydrogen sulphide together give a precipitate of mercuric sulphide. The molecular weight of the dissolved mercuric bromide was found to be 330.0—351.4 by the boiling-point method.

Mercuric iodide dissolves in ethyl acetate to the extent of 1 part in 68.03 at 18°, and has the molecular weight 413.7—442.3. Hydrogen sulphide gives a yellowish-red precipitate, which probably has the composition $\text{HgI}_2 \cdot 2\text{HgS}$. No precipitate is produced with ammonia. Ammonia and hydrogen sulphide together give a precipitate of mercuric sulphide; at first the precipitate is black, but on continued passage of ammonia, it turns red.

Saturated solutions of potassium mercuri-iodide in ethyl acetate do not give a precipitate with either ammonia or hydrogen sulphide. With both these gases together a black precipitate is produced, which contains mercury and sulphur.

At 18° the saturated solution of cadmium iodide in ethyl acetate has $D_4^{18} = 0.9145$, and contains 1 part of solute in 54.3 parts of solvent.

With hydrogen sulphide it gives a yellow precipitate of the composition $\text{CdI}_2 \cdot 2\text{CdS}$. With ammonia the compound $\text{CdI}_2 \cdot 2\text{NH}_3$ is precipitated. Ammonia and hydrogen sulphide together produce a precipitate of cadmium sulphide mixed with ammonium hydrosulphide. Hydrogen chloride produced no precipitate, but a slight liberation of iodine. Chlorine gave a white, flocculent precipitate of cadmium chloride, as also did mercuric chloride and bismuth trichloride. Bromine gave a dark-coloured liquid, but there was no evidence of reaction.

At 18° a saturated solution of stannous chloride in ethyl acetate contains 1 part of stannous chloride to 22.40 parts of ethyl acetate, and has $D_4^{18} = 0.9215$. With hydrogen sulphide a brown precipitate of stannous sulphide is produced, and with ammonia the compound $\text{SnCl}_2 \cdot 2\text{NH}_3$. Ammonia and hydrogen sulphide together give a precipitate of stannous sulphide mixed with ammonium hydrosulphide. Hydrogen chloride produces no precipitate. Chlorine and bromine both give stannic salts. Mercuric chloride gives a white precipitate of mercurous chloride, even in the presence of excess of stannous chloride.

At 18° a saturated solution of antimony trichloride in ethyl acetate has $D_4^{18} = 1.7968$, and contains 1 part of solute to 16.97 parts of solvent. No precipitate is produced with hydrogen sulphide, but with ammonia the compound $\text{SbCl}_3 \cdot 3\text{NH}_3$ is produced. Ammonia and hydrogen sulphide together give a precipitate of antimony trisulphide mixed with ammonium hydrosulphide. There is no reaction with either hydrogen chloride, chlorine, bromine, iodine, mercuric chloride, or bismuth trichloride.

At 18° , 1 part of bismuth trichloride dissolves in 60.36 parts of ethyl acetate, and the solution has $D_4^{18} = 0.9106$. When kept, the solutions become cloudy, owing to the formation of bismuth oxychloride. Hydrogen sulphide gives a precipitate of bismuth sulphide, and ammonia a precipitate of the composition $\text{BiCl}_3 \cdot 2\text{NH}_3$. Ammonia and hydrogen sulphide together give bismuth sulphide. Neither hydrogen chloride, chlorine, bromine, iodine, mercuric chloride, nor antimony trichloride have any action.

T. S. P.

Action of Heat on Aluminium in a Vacuum. ÉMILE KOHS-ABREST (*Compt. rend.*, 1910, 150, 169—173).—When aluminium is heated in a porcelain boat at 1100° in a vacuum, the metal is rapidly volatilised at first, but, after some hours, the loss in weight from this cause becomes negligible. After prolonged heating, the residue is found to be coated with a yellow film, consisting of an alloy of aluminium and silicon. The same results are obtained when boats of pure graphite are employed, but only when these are contained in a porcelain tube. The conclusion drawn is that aluminium vapour attacks the porcelain, liberating silicon, which is absorbed by the molten aluminium. The porcelain tubes employed are found to be coated internally with a black, crystalline deposit, from which the compound Al_2Si has been isolated.

W. O. W.

Synthetical Production of Sapphires by Fusion. AUGUSTE VERNÉUIL (*Compt. rend.*, 1910, 150, 185—187).—Hitherto, artificial

sapphires have been obtained which owed their colour either to chromium oxide or the iron oxide in a lower state of oxidation than ferric. Those coloured by chromium oxide were obtained by Sainte-Claire Deville and Caron in 1858—1865, but no one has been able to repeat their experiments. The sapphires coloured by iron oxide are of inferior quality.

The author finds that when alumina containing 1.5% of magnetic oxide of iron and 0.5% of titanous acid is fused in the oxyhydrogen flame, which has reducing properties, sapphires are produced which are identical in properties with the natural stones; the colour in this case is due to the presence of the oxides of iron and titanium.

T. S. P.

Do Clays and Cements Adsorb $\text{CO}_3^{=}$ Ions? JOH. D'ANS (*Zeitsch. Chem. Ind. Kolloide*, 1910, 6, 33—40. Compare Rohland, *Abstr.*, 1909, ii, 662).—In reference to the statement of Rohland that carbonates are adsorbed from solutions by cements, experiments were made in which weighed quantities of powdered cements and clays were agitated for several hours with a measured volume of a sodium carbonate solution. After filtration, the hydroxide and carbonate in the solution were determined.

The experimental data show that the dissolved carbonate is partly converted into hydroxide by the free calcium oxide of the cements. In a similar manner, ammonia is set free when the cements are agitated with a solution of ammonium chloride. On the other hand, the clays examined were found to have feebly acid properties, and, as a consequence, small quantities of sodium hydrogen carbonate were found in the solutions after agitation. The author's observations are considered to be incompatible with Rohland's view of carbonate adsorption.

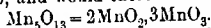
H. M. D.

Formation and Properties of Colloidal Manganese Dioxide. EUGEN DEISS (*Zeitsch. Chem. Ind. Kolloide*, 1910, 6, 69—77).—Stable colloidal solutions of manganese dioxide can be readily obtained by the reduction of permanganate solutions by means of dilute sodium arsenite. They can also be prepared by the oxidation of manganous salts if protective colloids are present in the solution. Various organic colloids can be used for the purpose, and it is also shown that colloidal ferric and aluminium hydroxides act as protective colloids if the amount of manganese in solution is relatively small. If larger quantities of manganese are present, ferric hydroxide behaves quite differently in that it favours the precipitation of the dioxide.

It is probable that the precipitation of manganese dioxide is always preceded by the temporary formation of a colloidal solution of the substance, coagulation resulting as a consequence of the presence of electrolytes. The formation of the iridescent flakes of manganese dioxide, which can be frequently observed in the oxidation or reduction of manganese compounds, is also attributable to the transient formation of a colloidal solution.

The so-called manganites must, in many cases, be regarded as adsorption compounds of manganese dioxide and bases. H. M. D.

The Thermal Formation of Manganates. I. OTTO SACKUR (*Ber.*, 1910, 43, 381—388).—A mixture of manganese dioxide with an excess of potassium carbonate was fused in a platinum crucible and maintained at a temperature slightly higher than the melting point of potassium carbonate. At the same time, air or oxygen, or carbon dioxide, or a mixture of these gases, was passed through the fusion by means of a platinum tube. From time to time portions of the fused mass were withdrawn by means of a tube of hard glass, and, after cooling, the percentages of available oxygen and of manganese were determined. The portions withdrawn were taken after the passage of gas had been stopped, and the manganese dioxide still unacted on had been allowed to sink to the bottom of the crucible. In one case the oxide, Mn_2O_4 , was used in place of the dioxide. The results show that the absorption of oxygen by the fusion ceases as soon as the atomic proportion of available oxygen to manganese becomes 1.6. This value is independent of the concentration of the manganese in the fusion, and of the partial pressure of the oxygen in the gas above the fusion, so that there does not exist an equilibrium between the different oxidation stages of manganese in the fusion and the oxygen in the gaseous phase, but a definite compound is formed which contains manganese and oxygen in the proportion of 1 : 2.6, and which would therefore have the formula



The fusion is dark green in colour. With a little water or with an alkaline solution, it gives a dark green solution (manganate) and a dark brown precipitate (MnO_2). With much water or dilute acids, a violet solution (permanganate) and manganese dioxide result.

A similar result was obtained when the potassium carbonate was replaced by potassium hydroxide, but with sodium carbonate the atomic proportion of available oxygen to manganese was 1.5 instead of 1.6. A mixture of potassium and sodium carbonates in equal proportions gave the same proportions as with sodium carbonate alone. The fusions containing sodium salts were grass-green in colour, as opposed to the dark green of the potassium compound. Calcium oxide gave similar results to sodium carbonate.

When oxygen is absorbed by the fusion, carbon dioxide is simultaneously evolved, as shown by the equation: $5MnO_2 + \frac{3}{2}O_2 + xK_2CO_3 = Mn_5O_{13} \cdot xK_2O + xCO_2$. By estimating the carbon dioxide evolved, it was found that the potassium compound formed in the fusion had the composition $Mn_5O_{13} \cdot 5K_2O$, whereas the sodium compound was $Mn_5O_{13} \cdot 2Na_2O$. The results obtained also showed that unless the oxygen was passed for a considerable time after the evolution of carbon dioxide had ceased, the compound formed in the fusion was $Mn_5O_{13} \cdot 5M_2O$, where M is either K or Na.

All the above results are only valid when an excess of alkali carbonate, sufficient to hold the manganese compound formed in solution and so permit of full oxidation, is used.

The complex compounds formed may be considered to be manganic manganates.

T. S. P.

The Thermal Formation of Manganates. II. Molecular-Weight Determinations in Fused Alkali Carbonates. OTTO SACKUR (*Ber.*, 1910, 43, 448—453).—The influence of dissolved salts on the melting points of potassium and sodium carbonates was determined by the method of cooling curves, using a platinum-platinum-rhodium thermocouple. The solutes used with potassium carbonate were potassium chloride, sodium chloride, and sodium carbonate, and with sodium carbonate, potassium chloride, sodium chloride, and potassium carbonate. In each case, with concentrations of the solute up to 1.2 gram-molecules per kilogram of the fusion, the lowering of the freezing point was proportional to the concentration of the solute. The molecular lowering for a binary salt which contains no ion in common with the solvent is approximately twice that for a salt containing a common ion. Ternary salts containing an anion common to the solvent have melting-point constants which are intermediate between those of the two classes of binary salts. These results are in accordance with the views of Goodwin and Kalmus (*Physical Review*, 1909, 28, 1).

The molecular lowering of the freezing point is 41° in potassium carbonate as solvent, and 31° in sodium carbonate. Sodium chloride dissolved in potassium carbonate is dissociated to the extent of 73%, and potassium chloride in sodium carbonate to 77%. The latent heats of fusion of potassium and sodium carbonates are calculated to be 66 and 82 cal. per gram respectively.

The molecular weights of the complex alkali manganic manganates dissolved in the alkali carbonates (see preceding abstract) were then determined. Pure manganese dioxide was melted with excess of the alkali carbonate and a current of gas consisting of $4/5$ oxygen: $1/5$ carbon dioxide passed through the fusion for some hours, after which time a portion was removed for analysis, and the melting point of the remainder determined. It was found, when oxidation was complete, that the ratio lowering of the melting point: concentration of the manganese in gram-atoms per 1000 grams of the fusion, was constant and equal to 43 in potassium carbonate and 35 in sodium carbonate. These results show that the solute in each case contains only 1 atom of manganese to the molecule, so that their formulae must be written K_2MnO_3 and Na_2MnO_3 respectively, that is, with a fractional number of atoms to the molecule. The full theoretical bearing of this result can only be properly discussed after further experimental results have been obtained.

T. S. P.

Cementation of Iron by Solid Carbon. GEORGES CHARPY and S. BONNEROT (*Compt. rend.*, 1910, 150, 173—175).—The experiments which have hitherto been made on the cementation of iron by solid carbon have been inconclusive, either because carbonising gases were not eliminated with certainty, or else because it was not proved that the iron and the carbon had been in intimate contact.

The authors proceed as follows: soft Martin steel, containing only traces of elements other than carbon and manganese, and carbon (pure sugar carbon, purified graphite, or clear white diamonds) were heated

in separate tubes in a vacuum to 1000° until practically no further gas (less than 0.1 c.c. per hour) was evolved, the pump working continuously. The iron and carbon were then brought into contact, with as little exposure to the air as possible, and again heated in a vacuum at 700° , which is below the temperature of rapid cementation, until the evolution of gas ceased. The temperature was then raised to 1600° and maintained at that temperature for several hours, the pump working continuously. In every case the results were negative; microscopic examination of the surface of the metal did not show the least trace of cementation. If, however, small quantities of gas were let into the apparatus, or if the pump was not continually worked, cementation took place, no matter what kind of carbon was used.

The adherence of carbon to iron under high pressures (3,000 atmos.) is very slight; hitherto, it has not been possible to carry out such experiments in a vacuum at high temperatures in order to ascertain if cementation is affected by the pressure.

If it be granted that carbon cannot penetrate into steel from the outside, except by means of some gaseous medium (carbon monoxide), it does not follow that the same thing holds for the diffusion of carbon to the interior of a casting or of steel. Fresh experiments in this direction are necessary.

T. S. P.

Metallic Tungsten. LUDWIG WEISS (*Zeitsch. anorg. Chem.*, 1910, 65, 279—340).—[With A. MARTIN.]—The aluminothermic reduction of wolframite is very violent, and an alloy is obtained, but by employing an insufficient quantity of aluminium, the reaction is moderated, and the product contains up to 90.66% W. A part of the iron and manganese can be removed by treatment with hydrochloric acid. It is not possible to reduce wolframite with zinc or magnesium, but heating with carbon in an arc furnace, followed by fusion with tungstic acid and calcium fluoride to remove carbon, gives a product containing only 0.24% C and 8.34% Fe.

Tungstic acid is best prepared by fusing wolframite with calcium carbonate and calcium chloride, and decomposing the product with acid. If magnesium carbonate is employed, the product contains large, red crystals of magnesium tungstate, which is not decomposed by acids. Tungstic acid may be readily electrolysed if mixed with cryolite, 250 amperes being employed at 13—14 volts. The metal is only obtained in globules, and contains 96% of tungsten. In order to raise the temperature, alumina may be added to the bath, the aluminium liberated reacting with the tungstic acid, but the product is still in a fine state of division. Experiments have also been made on the electrolysis of barium tungstate, and the reduction of calcium tungstate with aluminium. The best metal, containing 98.96% W, is obtained by fusing tungsten trisulphide with lime by means of an arc in a crucible of Acheson graphite.

[With A. STIMMELMAYR.]—Tungsten, fused in a hydrogen vacuum, is white and metallic; H 6.5—7.5, D 20 18.72. The malleability varies according to the heat treatment it has received. Small fragments may be hammered out. It is non-magnetic. The specific heat is 0.0358, and the heat of combustion of 1 gram is 1047 cal.

Tungsten forms coloured films, like steel, when heated in the air. Heating in oxygen converts it completely into the trioxide. Hydrochloric acid is without action; concentrated sulphuric and nitric acids and aqua regia only act slowly on the surface. Chlorine acts slowly; sulphur is without action. A mixture of nitric and hydrofluoric acids is the only reagent capable of dissolving the fused metal.

C. H. D.

Corrosion of Bronzes in Solutions of Electrolytes. FEDERICO GIOLITTI and O. CECCARELLI (*Gazzetta*, 1909, 39, ii, 557—575).—The authors have studied the corrosion of bronzes containing various proportions of tin, and subjected to different methods of cooling by means of 80 c.c. of *N*/10-hydrochloric acid containing 2% of ferric chloride. The losses in weight were determined after 169 and 366 hours, the results being compared with the aid of micrographs.

It is found that two bronzes of identical composition, after subjection to different thermal treatment, may exhibit quite different powers of resistance to corroding agents; such differences correspond with structural differences (compare Curry, *Abstr.*, 1906, ii, 756; Giolitti and Tavanti, *Abstr.*, 1908, ii, 946). Under similar conditions, the simultaneous presence in a bronze of the two α and β solid solutions, and especially of the products of segregation of these, accelerates the corrosive action. With bronzes containing not much more than 7% of tin, the velocity of corrosion increases with the proportion of the β -solution present, no matter whether such increased proportion is due to a different composition of the alloy or to different thermal treatment, such as altered velocities of solidification and of subsequent cooling. When the proportions of α and β solutions, and of their segregation products, remain constant, the velocity of corrosion is greater when the differences of concentration of the nuclei and margins of the separate mixed crystals of the two series are greater. As such differences of concentration are observable under the microscope, the degree of resistance of a bronze to corrosion may be determined beforehand by the same means.

T. H. P.

Metallic Zirconium. LUDWIG WEISS and EUGEN NEUMANN *Zeitsch. anorg. Chem.*, 1910, 65, 248—278. Compare this vol., ii, 33).—Crystallised potassium zirconium fluoride is mixed with purified sodium, covered with potassium chloride, and compressed into an iron vessel. After starting the reaction with a flame, it proceeds without further heating. The finely powdered metal thus obtained, is washed with alcohol, and boiled with hydrochloric acid. If washed with water first instead of alcohol, some oxide is always formed by the action of the sodium hydroxide produced on the metal. The zirconium may be compressed to form rods, which conduct electricity well, by high pressure without the use of binding material, but only globules of metal can be obtained in this way, as the rods break when a current is passed.

A better product is obtained by reducing the double fluoride with aluminium, forming the powdered regulus into rods, and heating in a specially constructed furnace in an atmosphere of nitrogen, preferably

under reduced pressure. The metallic zirconium, containing 99.8% Zr, is white, resembling cast-iron; it has $H\ 7-8$, $D^{18}\ 6.40$, and specific heat 0.0804.

Combustion in air only takes place at a very high temperature, and the formation of the dioxide is not complete unless oxygen is used. The heat of combustion of 1 gram is 1958.7 cal. It reacts with chlorine, forming the tetrachloride. Hydrogen at a red heat forms a grey hydride, ZrH_2 (compare Winkler, Abstr., 1890, 1372). When heated in oxygen, the hydride burns to *zirconium sesquioxide*, Zr_2O_3 , which is stable, and only burns slowly to the dioxide. C. H. D.

Natural Zirconium Earths. EDGAR WEDEKIND (*Ber.*, 1910, 43, 290—297. Compare Abstr., 1908, ii, 1046. [Compare Weiss and Lehmann, this vol., ii, 133]).—The author has investigated three varieties of a natural zirconium earth from São Paulo, in Brazil.

I. consisted of black, kidney-shaped masses of glassy appearance.

II. consisted of broken stones, varying in colour from dark brown to a light matt-grey; very often crystals of zirconium silicate were contained in it.

III. consisted of more or less rounded pebbles.

Analyses gave the following results:

	ZrO ₂	TiO ₂	Fe ₂ O ₃	SiO ₂ (free)	SiO ₂ (combined).	Total.
I.	94.12	0.98	3.22	0.43	1.93	100.73
II.	88.29	3.09	4.07	2.38	3.33	101.22
III.	74.48	1.35	10.26	14.08		100.17

The admixed ferric oxide could be removed mechanically from I.; it then contained 98% ZrO₂, and had $D\ 5.41$.

To obtain zirconium oxide free from iron, the filtered, acid, aqueous extract of the finely-powdered mineral was mixed with ammonia until a cloudiness resulted. Powdered ammonium carbonate was added until the precipitate first formed no longer dissolved. A further equal quantity of ammonium carbonate was then added, and the solution warmed to precipitate the iron. The warming was continued until a filtered portion of the liquid gave no coloration with sulphuric acid and hydrogen peroxide. The whole was then cooled, filtered, the filtrate acidified with sulphuric acid, and warmed to expel carbon dioxide, and the zirconium hydroxide precipitated with ammonia. The hydroxide was washed by decantation, and then converted into the oxide by heating.

To prepare the zirconium tetrahalogenides directly, the finely-powdered mineral was intimately mixed with excess of magnesium powder, and the mixture heated in a current of dry hydrogen. After treatment of the resulting mass with ammonium chloride, dilute hydrochloric acid, and warm dilute potassium hydroxide respectively, in order to remove the magnesium, magnesia, iron, and silicon, the residue was dried in a current of hydrogen and then heated in a stream of either chlorine or bromine. The corresponding tetrahalogenide sublimes.

The broken stones and pebbles were found to contain carbon

dioxide, nitrogen, hydrogen, oxygen, helium, and traces of argon, the broken stones containing the most gas. The mineral has been found by Gockel to be radioactive (Abstr., 1909, ii, 956), and he concluded that thorium was present. This element has, however, not yet been detected in any of the author's specimens.

T. S. P.

Physical and Chemical Properties of some Varieties of Antimony Trisulphide. VITO ZANI (*Bull. Acad. roy. Belg.*, 1909, 1169—1182. Compare Guinchant and Chrétien, Abstr., 1904, ii, 538, 568, 644).—The varieties examined were (1) the orange-red form produced by precipitation; (2) the greyish-black form obtained by heating the orange-red modification, and (3) natural stibnite.

The conclusions arrived at are (a) that all three forms have the formula Sb_2S_3 , and (b) that their specific gravities are 4.1205, 4.2906, and 4.6353 respectively. The first form gradually changes into the second on heating, and determinations made in various ways agreed in indicating 217° as the temperature at which transformation to the second form occurs with the development of heat. The changes of weight observed on heating the orange-red sulphide at about 100° are not due, as generally supposed, to loss of water, but to secondary reactions involving first the absorption of oxygen, then the loss of sulphur dioxide, and the eventual production of some metallic antimony. Stibnite seems to differ from the second form only in specific gravity.

T. A. H.

Mineralogical Chemistry.

Mineralogy of Franklin Furnace, New Jersey. CHARLES PALACHE (*Amer. J. Sci.*, 1910, [iv], 29, 177—187).—*Arsenopyrite*, brilliant crystals from limestone, gave anal. I (by E. C. SULLIVAN). The associated iron-pyrites contains about the same proportion of cobalt, but the associated pyrrhotite contains no cobalt and only a trace of nickel:

	Fe.	Co.	As.	S.	Total.
I.	32.48	1.16	48.72	18.80	101.16

Fluorite, pale red and granular, the matrix of franklinite grains, gave II (by G. STEIGER). The deficiency is probably fluorine, but even then there is not quite enough for the formula CaF_2 :

	Ca.	Mg.	Fe.	Mn.	Al.	F.	Cl, CO_2	Total.
II.	51.21	0.24	0.27	0.69	0.13	15.85	nil	97.84

Manganosite (III, by G. Steiger) forms a granular aggregate with franklinite and zincite; the irregular grains are dark green and have a cubic cleavage, being emerald-green in thin flakes; D 5.864; formula MnO . This rare species has previously been found only in Sweden.

Gahnite, variety *dysluite* (IV, by W. T. SCHALLER), large crystals from Sterling Hill; D 4.56.

Franklinite (V, by W. T. Schaller), small crystals of cubo-octahedral habit and adamantine lustre, and showing a deep red colour on edges or where splintered; D 5.09.

Heterolite (VI, by W. T. Schaller); under the microscope it is seen to be tetragonal with indistinct prismatic cleavages; D 4.85. This hitherto doubtful mineral may be described as a zinc hausmannite, $\text{ZnO} \cdot \text{Mn}_2\text{O}_3$ (hausmannite being $\text{MnO} \cdot \text{Mn}_2\text{O}_3$).

Pyrozenes: *jeffersonite* (VII, by G. Steiger) and *schefferite* (VIII, by W. T. Schaller).

Bementite (IX, by G. Steiger) is orthorhombic with three pinacoidal cleavages. The water is expelled only at a red-heat, and the formula $\text{H}_2\text{Mn}_2(\text{SiO}_4)_4$ shows a relation to tephroite ($\text{Mn}_2\text{Si}_4\text{O}_{16}$).

Friedelite (X, by W. T. Schaller), scales and indistinct, tabular, rhombohedral crystals. Formula $\text{H}_2(\text{MnCl})\text{Mn}_2(\text{SiO}_4)_6$, or, perhaps, $\text{H}_{20}(\text{MnCl})\text{Mn}_{14}\text{Si}_{14}\text{O}_{49}$.

Vesuvianite, variety *cyprine* (XI, by G. Steiger), bluish-green, fibrous; D 3.451; formula $\text{H}_2(\text{Al}, \text{Fe})_6\text{Ca}_{12}\text{Si}_{10}\text{O}_{45}$.

Cuspidine (XII, by C. H. WARREN), glassy, white, crystal fragments; D 2.965—2.989; formula $\text{Ca}_2\text{Si}(\text{O}, \text{F}_2)_4$. This species has hitherto been known only from Vesuvius.

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	Mn_2O_3	ZnO	CaO	MgO	H_2O (105°)	H_2O (>107°)	Total (loss 0.6% F.)
III.	—	—	0.26	—	94.59	1.80	3.41	—	0.11	0.38	0.10	100.45
IV.	1.47	47.27	0.90	—	0.93	—	87.10	1.01	1.09	1.21	—	100.26*
V.	—	—	66.58	—	0.96	—	20.77	0.48	0.34	0.71	—	97.91†
VI.	1.71	—	0.77	—	60.44	—	33.49	—	—	2.47	1.42	100.21
VII.	49.03	0.86	4.22	3.95	7.91	—	7.14	19.88	5.81	0.69	0.79	100.11
VIII.	49.50	0.26	1.46	1.61	9.69	—	trace	21.07	12.35	1.55	1.31	99.87‡
IX.	38.36	0.56	0.11	4.94	39.22	—	2.93	0.42	3.35	0.60	5.01	99.79
X.	34.69	—	—	1.45	48.40	—	1.05	0.63	0.98	1.94	0.08	100.48§
XI.	86.41	17.35	1.56	—	1.73	—	1.74	33.21	1.38	0.24	3.51	100.06
XII.	32.36	—	—	—	0.71	—	—	61.37	—	—	—	99.65

* Including CO_2 , 0.38. † State of oxidation of iron and manganese not known. ‡ Including Na_2O , 0.9; CO_2 , 0.43. § Including Cl , 3.49. || Including CuO , 1.85; PbO , trace; Na_2O , 0.44; K_2O , 0.50. ¶ Including Na_2O , 0.45; K_2O , 0.27.

Crystallographic descriptions are also given of *zincite* ($a:c = 1:1.5870$); *nasonite* (hexagonal, $a:c = 1:1.3167$); *glaucochroite* ($a:b:c = 0.4409:1:0.5808$); *willemitite* ($a:c = 1:0.6612$); *datolite*; *humite*, and *leucophaneite* ($a:b:c = 1:10.45:1:2.3155$; $\beta = 76.44^\circ$).

Ninety-three species of minerals are recorded from this locality, several of them now for the first time.

L. J. S.

Bismite. WALDEMAR T. SCHALLER and FREDERICK L. RANSOME (*Amer. J. Sci.*, 1910, [iv], 29, 173—176).—Bismite occurs in the oxidised zone in several mines in the Goldfield district of Nevada. It has the form of minute, pearly scales, with a brilliant, almost metallic lustre and a silvery whiteness. It encrusts the cavity-walls of spongy limonite and quartz, and has been derived by the alteration of bismuthinite (Bi_2S_3). Under the microscope the thin, colourless scales show a hexagonal outline with triangular markings on the base,

and a negative uniaxial interference-figure; there is a perfect basal cleavage. The crystals are therefore rhombohedral, $a:c=1:0.5775$. (Artificial crystals of bismuth trioxide are orthorhombic.) Analysis of material mixed with much gangue (mainly quartz) gave:

Bi_2O_3	H_2O (loss on ignition).	Fe_2O_3	Insoluble in HCl .	Total.
17.04	3.98	0.36	78.94	100.30

These results indicate that the crystals are either bismite (Bi_2O_3) or a hydrous bismuth oxide. If the latter be the case, the mineral is a new species (providing, of course, that Bi_2O_3 is the correct formula for bismite or bismuth ochre).
L. J. S.

Variety of Cobaltiferous Calcite from Capo Calamita, Elba.
FEDERICO MILLOSEVICH (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 91—92).—The author describes a sample of vivid red calcite occurring in crystalline masses on a limonitic and partly magnetitic rock. It is slightly harder than normal calcite, has $D\ 2.75$, and has the following composition:

CaO	CoO	FeO	MgO	MnO	CO_2	Total.
54.41	1.27	0.15	0.27	trace	43.55	99.65

which corresponds with: $\text{CaCO}_3\ 97.16$; $\text{CoCO}_3\ 2.02$; $\text{FeCO}_3\ 0.24$, and $\text{MgCO}_3\ 0.56$. The name *cobalto-calcite* is given to the mineral.

T. H. P.

The Plumboniobite Earths. ORRO HAUSER (*Ber.*, 1910, 43, 417—419).—Spectroscopic examination of the plumboniobite described in a previous communication (*Abstr.*, 1909, ii, 676) shows that the formula therein given must be modified to $\text{R}_2''\text{Nb}_2\text{O}_7\text{R}_2''(\text{Nb}_2\text{O}_7)_3$, where R'' represents Pb, Fe, UO, and Ca, and R''' represents Y, Gd, Yb, and Al.
T. S. P.

A Uranium Ore from German East Africa. WILLY MARCK-WALD (*Landw. Jahrb.*, 1909, 38, *Erganz. band V.*, 423—425, *Thiel Festschrift*).—An account of the methods employed, with the tabulated results of the analysis of a mineral found in German East Africa containing 80—90% uranium oxides ($\text{UO}_3=45\%$, $\text{UO}_2=39\%$) and 7—8% lead oxide (PbO).
F. M. G. M.

Minerals from the Pegmatites of Madagascar. LOUIS DUPARC, R. SABOT, and M. WUNDER (*Arch. Sci. phys. nat.*, 1910, [iv], 29, 62—71).—The pegmatite veins in the neighbourhood of Antsirabé are intrusive into quartzites and gneisses; they consist mainly of quartz and orthoclase, with some mica and various accessory minerals (tourmaline, beryl, spodumene, garnet, etc.) in large crystals of gem-quality. Usually the pegmatite is much decomposed.

Spessartite (anal. I), of gem-quality and honey-yellow or brown in colour, occurs in pegmatite at Tsilaïsa; refractive index (Na), 1.79980.

Cordierite (anal. II) was found as irregular fragments in the

micaceous quartzite of the Ibity range; refractive indices, $\alpha = 1.53958$, $\beta = 1.54516$, $\gamma = 1.54853$.

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	CaO	MgO	TiO ₂	Loss on ignition	Total	Sp. gr.
I.	35.76	21.06	1.78	—	39.40	1.23	0.46	0.10	—	99.79	4.0586
II.	49.05	33.08	0.83	4.38	—	—	11.04	—	1.64	100.02	2.5933

Crystallographic descriptions are also given of large zoned (red and brown) crystals of tourmaline from several localities. These crystals are optically biaxial with a small axial angle; refractive indices are given.

L. J. S.

Chemico-physical Investigations and Analysis of the Iron- and Arsenic-containing Water of Roncegno. RAFFAELLO NASINI, MARIO GIACOMO LEVI, and F. AGENO (*Gazzetta*, 1909, 39, ii, 481—512).—The results of the authors' chemico-physical measurements on this water are as follows: D_4^{20} 1.00293; freezing point, -0.10° ; osmotic pressure, $P = 1.205$ atmos.; specific electrical conductivity, $K_{25} = 0.00453$; radioactivity, intensity of saturation current, $I = 167.8 \times 10^{-15}$ amperes. The large amount of arsenic renders the full analysis interesting. The dissolved matter, in grams per litre, is as follows:

CuO	FeO	Fe ₂ O ₃	Al ₂ O ₃	MnO	NiO	CoO
0.01463	0.01006	1.21230	0.26670	0.01952	0.00325	0.00235
CaO	MgO	Na ₂ O	K ₂ O	SO ₂	SiO ₂	P ₂ O ₅
0.53919	0.11400	0.01109	0.00325	3.53880	0.13160	0.00750
As ₂ O ₃	As ₂ O ₅	NH ₃	Cl	Li ₂ O	TiO ₂	Residue at 100°
0.00350	0.05744	0.00027	0.00007	Trace	Trace	7.1610
						Residue at 150°
						6.5550

T. H. P.

Physiological Chemistry.

Narcosis and Want of Oxygen. II. The Effect of Deprivation of Oxygen on the Resting Current of Frog's Skin. G. MANSFIELD (*Pflüger's Archiv*, 1910, 131, 457—464).—Alcock has shown that narcotics of the fatty series abolish or lessen the secretion current of the frog's skin, but only if the narcotic is applied to its outer surface. Deprivation of oxygen acts in exactly the same way, and this is considered to support the theory that the narcotics in question produce their effects by lessening the supply of oxygen to the cell lipoids.

W. D. H.

Gaseous Metabolism of the Dog's Heart during Vagus Inhibition. J. M. WOLFSOHN and L. W. KETRON (*Proc. Amer. physiol. Soc.*, 1909, 25—26; *Amer. J. Physiol.*, 25).—The gases of the blood were analysed by the use of the mercury pump, and Barcroft and

Dixon's results were confirmed that vagus inhibition lessens the oxygen absorbed and the carbon dioxide produced, the latter being the more marked.

W. D. H.

The Inhibition of Soap Hæmolysis. WILHELM MEYERSTEIN (*Arch. exp. Path. Pharm.*, 1910, 62, 145—155).—The hæmolysis produced by soaps is inhibited by cholesterol and also by two other lipoids, kephalin and cerebrin. Sodium stearate and palmitate, which possess hæmolytic properties, increase the hæmolysis produced by sodium oleate. Alcoholic extracts of organs inhibit hæmolysis produced by soaps and by saponin. Dissolved red corpuscles protect other red cells from the solvent action, probably by the fact that lipoids are liberated.

W. D. H.

Observations on the Inhibitory Influence Exerted by Hypertonic Saline Solutions and Calcium Chloride Solutions on the Action of Specific Hæmolysins with Suggestions as to the Therapy of Blackwater Fever. W. D. SUTHERLAND and DAVID MCCAY (*Bio-Chem. J.*, 1910, 5, 1—22).—In blackwater fever the corpuscles are more vulnerable than in the normal state, and the liberation of hæmoglobin is due to a hæmolysin. Salts which decrease the number of inorganic ions in the plasma are recommended, for such salts to a large extent inhibit hæmolysis *in vitro*. The intravenous injection of a mixture of sodium chloride and calcium chloride is recommended.

W. D. H.

Action of Biotoxin on Blood. FRANCESCO MARINO-ZUCCO and L. GHUGANINO (*Gazzetta*, 1909, 39, ii, 586—616).—Further experiments on the toxin previously described (*Abstr.*, 1904, ii, 754) give the following results. The biotoxin, as the authors term it, has an energetic poisoning effect on the blood, its action, which can be followed by means of the spectroscope, being as follows. The oxyhæmoglobin is resolved by the action of the enzyme into two principal substances, one of which has a protein character and contains all the iron of the hæmoglobin, the other being a non-protein pigment which is apparently analogous to the colouring matter of the bile and exhibits a spectrum characterised by a band in the red, $\lambda = 650-632$, and another between the blue and green, $\lambda = 520-490$. This action on the blood pigment is so sensitive that, by means of the spectroscope, the presence of one five-millionth ($1/5,000,000$) of the biotoxin in 1 c.c. of 10% defibrinated blood solution can be recognised. In small proportions the biotoxin occurs in circulating blood, its presence being demonstrated, not only by direct extraction, but also by the changes taking place in sterilised blood solutions when these are maintained for three months at $40-41^\circ$ (the optimum temperature of the toxin) or for a longer period at the ordinary temperature.

T. H. P.

Influence of Alcohol on Metabolism. LAFAYETTE B. MENDEL and WARREN W. HILDITCH (*Proc. Amer. physiol. Soc.*, 1909, 11; *Amer. J. Physiol.*, 25).—The most marked result of alcohol as revealed by urinary analysis is to increase the amount of purine

substances. "Protein sparing" so frequently observed before was also shown to occur. The paucity of the results indicates that the body can maintain its catabolic functions along normal channels, despite the interference of toxic agents, a factor of safety being present. In the more marked conditions of alcoholism, conjugated glycuronates may be excreted both in men and animals; these disappear with the cessation of the intake of alcohol.

W. D. H.

Relation of Pancreas to Sugar Metabolism. WESLEY M. BALDWIN (*Proc. Amer. physiol. Soc.*, 1909, 21—22; *Amer. J. Physiol.*, 25).—Experiments with the muscles and pancreas of cats, frozen solid by liquid air and then powdered, show that when extracts are made, the presence of the pancreas increases glycolysis in an alkaline medium, and thus the original statements of O. Cohnheim are confirmed.

W. D. H.

Digestion of Inulin. H. BIEBRY (*Compt. rend.*, 1910, 150, 116—118).—In the higher animals, transformation of inulin is effected by the hydrochloric acid of the gastric juice, and is not due to the presence of a soluble pancreatic ferment. The pancreatic juice of dogs is incapable of effecting hydrolysis. The gastro-intestinal secretion of *Helix pomatia*, however, slowly hydrolyzes inulin with formation of levulose.

W. O. W.

Effects of Carbohydrates on the Artificial Digestion of Casein. NELLIE E. GOLDTHWAITE (*J. Biol. Chem.*, 1910, 7, 69—82).—Carbohydrates retard the digestion of caseinogen *in vitro*, in proportion to the amount added.

W. D. H.

Chemical and Bacteriological Study of Fresh Eggs. MARY E. PENNINGTON (*J. Biol. Chem.*, 1910, 7, 109—132).—In fifty-seven eggs, seven only were sterile; in the remainder, bacteria, of which thirty-six varieties were identified, were present both in white and yolk. The chemical data relate mainly to nitrogenous compounds in both white and yolk—nitrogen coagulable by heat, in filtrate, in tannic acid precipitate, etc. These details are given in numerous tables.

W. D. H.

The Phosphorus-content of Growing Dogs. ALEXANDER LIPSCHÜTZ (*Arch. exp. Path. Pharm.*, 1910, 62, 210—243).—In growing dogs, restriction of the diet to rice and white of egg leads to a relative "phosphorus hunger," the body containing only from one-sixth to one-fifteenth of the normal amount of phosphorus. This diet, poor as it is in phosphorus, leads to changes in the skeletal system similar to those found in the bones in "Barlow's disease," and to a slower rate of growth than normal.

W. D. H.

Irregularities of the Mammalian Heart under Aconitine. ARTHUR R. CUSHNY (*Heart*, 1909, 1, 1—22).—From experiments on dogs, in which aconitine in 0.05 mg. doses was injected intravenously, it was found that several forms of cardiac irregularity could be pro-

duced, among which impaired conduction through the auriculo-ventricular bundle may be mentioned. Aconitine has a greater tendency to cause *pulsus alternans* than most other poisons.

W. D. H.

Influence of the Pancreas on the Glycolytic Power of Muscle. G. C. E. SIMPSON (*Bio-Chem. J.*, 1910, 5, 126—142).—By incubation of muscle juice or extract, especially in the presence of pancreatic juice, large amounts of reducing substances are formed, possibly from glycogen, but more largely from autolytic or tryptic digestion of the muscle plasma. The nature of these substances has still to be investigated. The difficulty of maintaining asepsis is, however, almost insuperable, and the difficulty of estimating sugar in the presence of large amounts of proteins leads to great experimental error. So far as observations are possible under these limitations, the glycolysis obtained by the combined action of pancreatic and muscle juices is believed to be not, as a rule, greater than the sum of the actions of the constituents of the mixture.

W. D. H.

The Silicic Acid in Whartonian Jelly. HUGO SCHULZ (*Pflüger's Archiv*, 1910, 131, 447—456).—Frauenberger (Abstr., 1908, ii, 969) having thrown doubt on the statements of the author regarding silicic acid in the Whartonian jelly of the human umbilical cord, the experiments in question have been repeated, and the results are practically the same as in the previous investigation (Abstr., 1902, ii, 275), namely, that the jelly contains 4% of ash, not 11.6% as stated by Frauenberger, and that 1 kilogram of the dried jelly contains 0.24 gram of silica.

W. D. H.

The Parent Substance of Glycogen. EDUARD PFLÜGER and PETER JUNKERSDORF. Postscript. EDUARD PFLÜGER. Influence of Phloridzin on the Sugar in the Blood. PETER JUNKERSDORF. Estimation of Glycogen in the Tortoise's Liver. EDUARD PFLÜGER (*Pflüger's Archiv*, 1910, 131, 201—301, 302—305, 306—313, 314—316).—The first paper contains protocols of over 150 experiments on dogs. The liver was rendered almost free from glycogen by means of phloridzin and inanition; but twenty-four hours later, if no more phloridzin is given, the liver may contain as much as 3% of glycogen; the mean percentage in thirty-eight experiments was 1.1%. If cod's flesh is given, the percentage rises enormously, and the conclusion is drawn that this is not a "sparing" phenomenon, neither is the glycogen derived from fat, but from protein. In fact, this is regarded as the first absolute proof of the origin of carbohydrate from protein. Excessive doses of protein food do not increase the percentage of glycogen so much as moderate doses.

In the postscript, a few experiments given seem to indicate that glycine may act as a parent substance of glycogen, but these are to be repeated on a larger scale.

The third paper confirms the previously well-known fact that in phloridzin diabetes the amount of sugar in the blood is not higher than normal: it may be lower.

Pflüger's method of estimating glycogen has been tested already in thousands of cases; the tortoise's liver, however, does not lend itself, for certain unexplained reasons, to the method; in this case, therefore, reliance has to be placed on a previous method which is not so exact.

W. D. H.

Physiology of Lymph. X. The Comparative Electrical Conductivity of Lymph and Serum, and its Bearing on Theories of Lymph Formation. A. B. LUCKHARDT (*Amer. J. Physiol.*, 1910, 25, 345—353).—Several observers have stated that lymph contains more chlorides than serum; this is confirmed by the electrical conductivity method. The serum is certainly richer in protein than lymph, but the increase of protein (as shown by experiments on white of egg) is inadequate to explain the lesser conductivity of the former fluid. Fat droplets in the chyl depress the conductivity of lymph. A 10% increase in the amount of sodium chloride in physiological saline solution produces an effect on conductivity comparable to that seen in comparing lymph and serum. The excess of chlorides awaits explanation, and is not compatible with purely mechanical theories of lymph formation.

W. D. H.

Physiology of Lymph. XI. The Fractional Coagulation of Lymph. HERBERT O. LUSKY (*Amer. J. Physiol.*, 1910, 25, 354—366).—Lymph may coagulate in successive crops of fibrin; this will depend on the amount of thrombin present. In lymph the conversion of prothrombin into thrombin by calcium appears to occur very slowly. A small yield of fibrin with a small amount of ferment in a given time is no proof that thrombin is not an enzyme, as Rettger (*Abstr.*, 1909, ii, 680) considers. The time factor was neglected by this observer; after the lapse of a longer time, as much fibrin may be formed as in other specimens is formed by larger amounts of the enzyme in a shorter time.

W. D. H.

Presence in Cow's Milk of an Anæroxydase and a Catalase. J. SARTHOV (*Compt. rend.*, 1910, 150, 119—121. Compare this vol., ii, 57).—Polemical against Bordas and Touplain (*loc. cit.*). The author quotes the results of experiments which appear to show that the catalytic actions brought about by filtered milk are due not to casein, but to lactic ferments.

W. O. W.

Reactions of Curdled Milk due to the Colloidal State. FRÉD. BORDAS and F. TOUPLAIN (*Compt. rend.*, 1910, 150, 341—343. Compare this vol., ii, 57).—The authors consider that the reactions of curdled milk, hitherto attributed to the presence of enzymes, may be explained by the colloidal state of the casein. Colloidal solutions of ferrous oxalate or ferric lactate are found to give all the catalytic reactions of curdled milk, decomposing hydrogen peroxide, for example, and developing a blue coloration with *p*-phenylenediamine. Curdled milk which has been heated to 110° and cooled gives no reaction with these substances; if, however, the casein is brought to a very finely-divided state by allowing a jet of the liquid under a pressure

of 300 atmospheres to impinge on an agate plate, it becomes endowed with marked catalytic properties.

W. O. W.

The Phosphorus in Faeces. ALEXANDER LIPSCHITZ (*Arch. exp. Path. Pharm.*, 1910, 62, 244—252).—The normal faeces of the growing animal (dog and man) are poorer in phosphorus than in the adult condition.

W. D. H.

The Degradation of Fatty Acids in Diabetes mellitus. JULIUS BAER and LEON BLUM (*Arch. exp. Path. Pharm.*, 1910, 62, 129—138. Compare Abstr., 1908, ii, 1057).—It has been shown previously by the authors that the administration of butyric acid, hexoic acid, β -methylbutyric acid, β -ethylbutyric acid, leucine, phenyl-alanine, and tyrosine to diabetics causes an increase of β -hydroxybutyric acid, and members of that group in the body that constitutes acidosis. Stress is laid on the importance of the β -position in the substances given. The present research relates mainly to leucine; *d*-leucine produces no effect, but the naturally occurring *l*-leucine is effective in the direction above indicated. Embden states that by perfusing the liver with *d*-leucine, acetone formation is observed, and that this does not occur with *l*-leucine. These experiments were repeated, but no marked difference could be observed between the two isomerides.

W. D. H.

Formation of Glycogen in the Liver of Tortoises with Pancreatic Diabetes. M. NISHI (*Arch. exp. Path. Pharm.*, 1910, 62, 170—179).—The blood of normal tortoises contains no reducing substance; total extirpation of the pancreas leads to intense glycaemia and glycosuria; in this condition perfusion of the liver with a solution of dextrose leads to glycogen formation there as in normal animals.

W. D. H.

The Production of Sugar from Amino-acids. A. I. RINGER and GRAHAM Lusk (*Proc. Amer. physiol. Soc.*, 1909, 19; *Amer. J. Physiol.*, 25).—Both glycine and alanine administered to dogs suffering from phloridzin glycosuria are completely converted into sugar; and three of the four carbon atoms in aspartic acid, and three of the five in glutamic acid, are similarly convertible into dextrose.

W. D. H.

Phloridzin Glycocholia. R. T. WOODYATT (*J. Biol. Chem.*, 1910, 7, 133—136).—The administration of phloridzin leads to presence of sugar, not only in the urine, but also in the bile; its action is, therefore, not confined to the kidneys.

W. D. H.

Acapnia and Shock. V. Failure of Respiration after Intense Pain. YANDELL HENDERSON (*Amer. J. Physiol.*, 1910, 25, 385—402. Compare this vol., ii, 137).—A continuation of work along the same lines as in previous papers. The point specially insisted on is that serious and even fatal apnoea may be a result of intense pain, and a case in support of this view in a man, is recorded.

W. D. H.

* **Antagonistic Action of Barium and Magnesium.** DON R. JOSEPH and SAMUEL J. MELTZER (*Proc. Amer. physiol. Soc.*, 1909, 17—18; *Amer. J. Physiol.*, 25).—[In rabbits, 1·2 grams of magnesium sulphate per kilo. of body-weight are fatal. It has been previously shown that these effects are antagonised by calcium salts. The effect on the respiration is also antagonised by barium salts, although the animal remains anaesthetised and otherwise paralysed. The same dose of barium chloride alone is fatal, so that the toxic effects of barium are antagonised by magnesium.]
W. D. H.

The Increase of Susceptibility to Adrenaline Produced by Cocaine. ALFRED FRÖHLICH and OTTO LOEWI (*Arch. exp. Path. Pharm.*, 1910, 62, 159—169).—Small inactive doses of cocaine increase markedly the intensity and duration of the effects of adrenaline on the blood-vessels, eye, and bladder. The combination of the two is therefore recommended for therapeutic use.
W. D. H.

Fate of Sodium Benzoate in the Human Organism. HENRY D. DAKIN (*J. Biol. Chem.*, 1910, 7, 103—108).—Sodium benzoate in doses of 5 to 10 grams a day for two or three days is wholly eliminated in the urine as hippuric acid. The increase of glyconic acid derivatives is trifling. These results confirm those of Lewinski (*Abstr.*, 1908, ii, 518; 1909, ii, 820), and are in opposition to those of Brugsch and Tsuchiya (*Zeitsch. exp. Path. Ther.*, 1909, 5, 337). An improved method of hippuric acid estimation is described.
W. D. H.

The Action of Ether on the Circulation. E. H. EMBLEY (*Bio-Chem. J.*, 1910, 5, 79—93).—Ether administered with plenty of air lowers the blood-pressure; in high concentration it paralyses the heart muscle. It stimulates the inhibitory mechanism of the heart, and relaxes the arterioles. It is in every way safer than chloroform.
W. D. H.

The Chemistry and Bio-chemical and Physiological Properties of a Sapo-glucoside obtained from the Seeds of *Bassia longifolia* (Mowrah Seeds). BENJAMIN MOORE, MISS S. C. M. SOWTON, F. W. BAKER-YOUNG, and T. ARTHUR WEBSTER (*Bio-Chem. J.*, 1910, 5, 91—125).—The sapo-glucoside in question is named *mowrin*. Directions for its isolation are given; on hydrolysis, it yields *mowric acid*, furfuraldehyde, and dextrose. It is very toxic, and workers with Mowrah meal suffer from virulent cellulitis of the hands and feet. Details are given *inter alia* of its haemolytic action, and of its action on the heart; in the latter relation it resembles drugs of the digitalis group.
W. D. H.

Comparative Action of Stovaine and Cocaine as Measured by their Direct Effect on the Contractility of Isolated Muscle. VICTOR H. VELEY and AUGUSTUS D. WALLER (*Proc. Roy. Soc.*, 1910, B, 82, 147—151).—Stovaine, methylstovaine, and cocaine have approximately equal affinity values as measured by the methyl-orange

and borax precipitation methods. Measured by Waller's method, the toxicities of these drugs to plain muscle are also equal. G. S. W.

Toxicity of Thallium Salts. ROBERT E. SWAIN and W. G. BATEMAN (*J. Biol. Chem.*, 1910, 7, 137—151).—The toxicity of thallium salts has been a matter of divergence of opinion. The present experiments on numerous species of animals show that it is among the most toxic of the elements. The symptoms closely resemble those of uræmic poisoning, but the kidneys so far examined show no very severe changes. W. D. H.

Mercury and Hirudin. Mlle. GUSTAVA PRUSSAK (*Arch. exp. Path. Pharm.*, 1910, 62, 201—209).—The toxic action of mercury (given as sublimate) is much increased by the administration of hirudin; the minimal lethal dose of the former is thus lessened. The same symptoms and pathological appearances occur as when the blood is not rendered incoagulable by hirudin. W. D. H.

Cobra Poison and Hæmolysis. III. IVAR BANG (*Biochem. Zeitsch.*, 1910, 23, 463—498. Compare Abstr., 1909, ii, 681).—Although pure lecithin has no influence on the hæmolysis produced by cobra venom, it is shown that commercial lecithin acts as an activator under a number of different experimental conditions. This is explained by the hypothesis that the membrane of the corpuscles is rendered more permeable to salts, especially to their acid constituents, the lecithin combining with the alkali. It is further supposed that there are two receptors, and that the poison reacts with the second receptor in the presence of lecithin; it is this which renders the lipid membrane permeable. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Assimilation of Carbon by Bacteria which Oxidise Hydrogen. A. J. LEBEDEF (Ber. deut. bot. Ges., 1910, 27, 598—602).—The development of the microbe employed in a solution containing minerals and nitrate is coincident with an absorption of carbon dioxide, hydrogen, and oxygen, and a slight liberation of free nitrogen. The average result of about fifty experiments showed that for 100 c.c. of carbon dioxide used, 500 to 1500 c.c. of hydrogen were oxidised. The oxidation of hydrogen takes place, however, when carbon dioxide is absent, the hydrogen and oxygen being absorbed in the relation $H_2:O_2=2$.

In the autotrophic assimilation of carbon dioxide, the volume of oxygen liberated is equal to that of the carbon dioxide. The process is the same as that which takes place in green plants. In complete absence of free oxygen the process is slow. N. H. J. M.

Cellulose as Source of Energy in the Assimilation of Atmospheric Nitrogen. HANS PRINGSHEIM (*Centr. Bakt. Par.*, 1910, ii, 26, 222—227).—*Clostridium*, in conjunction with organisms which decompose cellulose, gives better results with cellulose than *Clostridium* alone with dextrose, sucrose, starch, lactose, or mannitol. The amount of nitrogen fixed depends on the concentration, being higher, per gram of substance fermented, the lower the concentration. With *Clostridium* + methane fermentation, the amounts of nitrogen fixed were 10.4 and 5.4 mg. per gram with 0.5 and 1%, whilst with *Clostridium* + hydrogen fermentation the amounts were 8.3 and 7.7 mg. respectively. *Azotobacter* + methane fermentation gave 4.5 mg. nitrogen per gram (0.5% cellulose).
N. H. J. M.

Agar-Agar as Source of Energy in the Assimilation of Atmospheric Nitrogen. HANS PRINGSHEIM and ERNST PRINGSHEIM (*Centr. Bakt. Par.*, 1910, ii, 227—231).—In a solution containing 0.2% agar and 0.04% dextrose inoculated with *Bacillus gelaticus* + *Clostridium Americanum*, 26.6 mg. of nitrogen were assimilated per gram of agar, whilst with a similar solution containing 0.005% of ammonium phosphate instead of dextrose, the amount of nitrogen fixed was 15.4 mg. per gram. Two experiments, in which solutions containing (1) 0.5% agar and 0.1% mannitol, and (2) the same proportion of agar and 0.04% mannitol, were inoculated with *B. gelaticus* + *Azotobacter chroococcum* resulted in the fixation of 14 and 6.8 mg. nitrogen respectively.

The results are of interest as they account for the origin of the nitrogen required by the vegetable and animal organisms in the sea. Benecke and Keutner (*Ber. deut. bot. Ges.*, 1903, 21, 333) showed that both *Azotobacter* and *Clostridium* occur in sea-water, and the present results indicate that the agar present in the red and brown Algae is rendered available as source of energy with the help of *Bacillus gelaticus*.
N. H. J. M.

Ammonia and Nitrates as Sources of Nitrogen for Mould Fungi. G. RITTER (*Ber. deut. bot. Ges.*, 1910, 27, 582—588).—The assimilation of ammonia by mould fungi is the more complete the weaker, and less poisonous, the acid liberated from the salt, and the development of the fungi on nutritive solutions containing ammonium salts is in direct proportion to their power of resisting the action of free acids.

Aspergillus niger and *Rhizopus nigricans* liberate considerably more acid than the amount which permits the germination of their spores, whilst with submerged fungi, such as the *Mucoraceae*, the amount of acid produced tends to be below the limit.

Aspergillus glaucus, *Mucor racemosus*, and *Cladosporium herbarum*, which are termed "nitrate" fungi (Laurent, *Ann. Inst. Pasteur*, 1888, 2, 593, and 1889, 3, 362), develop at least as well, and in part better, when supplied with ammonium salts as with nitrates. *Rhizopus nigricans*, *Mucor mucedo*, and *Thamnidium elegans* do not assimilate nitrates appreciably.
N. H. J. M.

Production and Utilisation of Nitrous Oxide by Bacteria. BRUNO TACKE (*Centr. Bakt. Par.*, 1910, ii, 26, 236. Compare Beyerinck and Minkmann, *ibid.*, 25, 30).—The author refers to a previous paper (*Landw. Jahrb.*, 1887, 16, 917) in which he showed the production of considerable amounts of nitrous oxide in denitrification experiments.

Nitric oxide may also be produced in considerable quantity. An experiment in which beet was fermented in a vacuum yielded so much nitric oxide in eight or ten days that red fumes were seen on opening the vessel.

N. H. J. M.

Influence of Depth of Cultivation on Soil Bacteria and their Activities. WALTER E. KING and CHARLES J. T. DORYLAND (*Kansas State Agric. Coll. Exper. Stat. Bul.*, 161, 1909).—Two plots, each 42 feet square, the one a silt loam, and the other a fine sand, were divided into six sub-plots, the soil of which was stirred to the depth of two, four, six, eight, and ten inches respectively, one sub-plot being left undisturbed. Samples were frequently taken, and the number of bacteria determined. The temperature of the soil was recorded, and the amount of moisture in the first twelve inches of soil determined each time.

The results showed that deep ploughing (eight to ten inches) increased the number of bacteria in both soils. It also increased the production of ammonia in the soil, whilst denitrification was decreased. The maximum number of bacteria was found within the fifth and sixth inches.

An excess of moisture in the soil reduces the number and diminishes the activity of the bacteria. There are, however, more or less regular periods of increased and diminished bacterial life and activity, to some extent independent of moisture and temperature, and due, perhaps, to the presence of bacterial by-products.

N. H. J. M.

New Theory of Alcoholic Fermentation. R. KUSSEROW (*Centr. Bakt. Par.*, 1910, ii, 26, 184—187).—The theory is essentially as follows: The yeast, requiring oxygen, reduces the sugar to a hexahydric alcohol, which decomposes into ethyl alcohol, carbon dioxide, and hydrogen. The nascent hydrogen causes a further reduction of sugar, followed by the decomposition of the alcohol, and this continues until the sugar is used up or until the fermentation is stopped by the oxidation of the hydrogen.

Fermentation is therefore first brought about by the reducing action of the living yeast cell, or by similarly acting organisms, whilst its continuation is purely chemical, depending on the production of hydrogen.

N. H. J. M.

Action of Ultra-violet Light on Wine During Fermentation. CHARLES MAURAIN and G. WARCOLLIER (*Compt. rend.*, 1910, 150, 343—344. Compare Abstr., 1909, ii, 752).—The sterilisation of white wine under the action of ultra-violet light takes place with greater rapidity than in the case of cider previously studied. Thus a

layer of wine, 1.7 mm. in thickness, is sterilised in thirty to sixty seconds when exposed at 4 cm. from a quartz-mercury lamp, whilst under the same conditions cider requires about fifteen minutes.

W. O. W.

Causes Favouring the Formation of Acetaldehyde in Wine. AUGUSTE TRILLAT (*Bull. Soc. chim.*, 1910, [iv], 7, 71-78).—In previous papers (Abstr., 1909, ii, 429, 606, 607) the author has shown that wine contains acetaldehyde, and has directed attention to the important influence of this constituent in the "ageing," "yellowing," and other changes which take place in stored wine. In the present paper the conditions under which aldehyde is formed are considered.

It is shown that wine agitated with air, or merely exposed to air, produces acetaldehyde more rapidly than an aqueous solution of alcohol of the same strength. The amount formed varies with the temperature and the nature of the containing vessel. Old wines contain more aldehyde than new ones. The amount of aldehyde is increased by the presence of yeast and other micro-organisms and by the addition of oxidising agents, and its formation is accelerated by iron (Abstr., 1909, ii, 429).

T. A. H.

Germicidal Action of Metals and its Relation to the Production of Peroxide of Hydrogen. ALLAN C. RANKIN (*Proc. Roy. Soc.*, 1910, B, 82, 78-87. Compare Barnes and Shearer, Abstr., 1908, ii, 344, 829).—The capacity of the pure metals, zinc, aluminium, and copper to destroy *Bacillus coli* suspended in an alkaline tap-water is associated with the coincident presence of oxygen and the solution of minute traces of the metals.

The simultaneous liberation of hydrogen peroxide in the case of the first two metals, although easily recognised, is not sufficient in amount to explain the germicidal action. In the case of copper no formation of hydrogen peroxide could be detected.

G. S. W.

Disinfection by the Incomplete Combustion of Straw. AUGUSTE TRILLAT (*Compt. rend.*, 1910, 150, 339-341).—The fumes produced during the limited combustion of straw in air owe their disinfectant properties to the presence of aldehydes and phenolic compounds. These appear to be produced by catalytic oxidation of alcohols, acetic acid, acetaldehyde, etc., in presence of finely-divided carbon. Formaldehyde, which has been recognised by its action on dimethylaniline, is formed to the extent of 0.002 to 2 grams per kilo. of straw. The results of experiments on bacteria are given, from which it appears that the germicidal action is well marked with pathogenic organisms, such as *Bacillus coli communis*, but that the fumes are less efficacious in the case of more resisting bacteria.

W. O. W.

Action of Aqueous Solutions of Electrolytes on Germination. HENRI MICHELIS (*Bull. Acad. roy. Belg.*, 1909, 1076-1118).—The first of two papers on the influence exerted by electrolytes on the

germination of seeds. Wheat was used for the experiments. The chief conclusions arrived at are as follows: The osmotic pressure of the solutions employed ($N/10$ to $N/1000$) did not influence the germination; the greater difference between the effects on germination of $N/10$ and $N/100$ solutions than between the effects of $N/100$ and $N/1000$ solutions is due not to greater differences in osmotic pressures of the solutions, but to greater differences in ionisation; the formation of root hairs is favoured by the presence of $-NO_3$ ions; the experimental evidence does not support the view that the growth of cells is due to the osmotic pressure of cell sap.

Wheat grains of about equal size were soaked in water for twenty-four hours, and then placed for a certain time on muslin lying in a solution of the electrolyte. At the end of this time the seedlings were removed, and the progress of germination determined by measuring (1) length of first leaf; (2) length of radicle; (3) average weight of seedling. The last of these factors for single electrolytes is given in the following table:

Concentration.	NaCl.	KCl.	KNO ₃ .	KHO.	Ca(NO ₃) ₂ .
$N/10$	0.133	0.130	0.115	-	0.126 gram
$N/100$	0.216	0.235	0.251	-	0.152 "
$N/1000$	0.211	0.211	0.315	0.225	0.221 "

$N/100$ solutions of potassium chloride and potassium nitrate are each more favourable to germination than mixtures of such solutions, whilst mixtures of sodium nitrate and potassium nitrate solutions ($N/100$) are more favourable than those of either salt alone. Previous investigations on the antagonistic action of sodium chloride to other salts (compare Coupin, Abstr., 1900, ii, 236; Michels, Abstr., 1907, ii, 124; Osterhout, this vol., ii, 62) as regards their influence on germination are extended, and the same action is shown to occur with strontium chloride, zinc sulphate, and barium chloride. T. A. H.

The Changes Taking Place in the Composition of Fruits which Ripen after being Gathered. RICHARD OTTO and W. D. KOEPER (*Zeitsch. Natur. Genussm.*, 1910, 19, 10—13).—Results of analyses are given showing the changes which take place in the chemical composition of certain fruits (*Prunus spinosa*, etc.) when the latter are allowed to ripen (nachreifen) after being gathered. It was found that the levulose increased from 14.44 to 21.00%, whilst the dextrose decreased from 16.04 to 10.75%, these results being calculated on the dry substance. The total acidity (as malic acid) decreased from 9.17 to 6.56%, and the tannin from 9.45 to 6.82%. The decrease in the amounts of acid and tannin was, therefore, much larger than the increase in the quantity of total sugar. The tannin appeared to be converted into an oxidised compound. The increase in the "sweetness" of the sloe-fruit during ripening thus seems to be due to a decrease in the amounts of acids and tannin present, and to the conversion of dextrose into levulose. W. P. S.

Microchemical and Physiological Studies on Tannin. LUIGI ERMANNO CAVAZZA (*Zeitsch. wiss. Mikroskopie*, 1909, 26, 59—64).—A tabulated record of the microchemical reactions shown by catechu.

caffetanric acid, pyrogallol, resorcinol, phloroglucinol, vanillin, quinol, and salicylic acid with ferric chloride, ammonium metavanadate, potassium hydroxide, potassium dichromate, tellurium carbonate, gold chloride, and palladium chloride. The tannates of indium, lanthanum, iridium, yttrium, palladium, and cerium were prepared.

A comparative study of the quantity of tannin contained in the leaves and in the branches of oak, chestnut, tamarisk, fir, and other forest trees at different periods of the year showed that the amount frequently varied inversely; the tannin content of the leaves reaching its maximum in September, that of the twigs in July and December.

F. M. G. M.

Choline Content of Certain Edible Fungi. KARL POLSTORFF (*Festschrift Otto Wallach*, 1909, 579—583).—Since choline is converted, under certain conditions, by micro-organisms into neurine (compare Schmidt, Abstr., 1892, 219), the proportion of choline in three common edible fungi, namely, *Cantharellus cibarius*, *Agaricus campestris*, and *Boletus edulis*, has been estimated and found to be present to the extent of 0.01%, 0.015%, and 0.0056% respectively. It is evident, therefore, that cases of poisoning arising from eating preserved fungi are not to be attributed to the action of neurine derived from choline.

W. H. G.

Presence of Gentiopicroin in *Chlora perfoliata*. ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1910, 150, 114—116; *J. Pharm. Chim.*, 1910, [vii], 1, 109—113).—Gentiopicroin has been isolated from *Chlora perfoliata*, in which it occurs to the extent of 1.5%. The product was found to be identical with the glucoside occurring in the yellow gentian.

W. O. W.

Occurrence of Betaines and Choline in Drugs containing Caffeine and Theobromine. KARL POLSTORFF (*Festschrift Otto Wallach*, 1909, 569—578).—Kola beans contain from 0.25 to 0.45% of betaine in addition to caffeine and small quantities of theobromine. Coffee beans contain about 0.2% of trigonelline, whilst choline is present in cocoa beans, Indian tea, and Pasta Guarana.

W. H. G.

Presence of an Alkaloid in the Seeds of *Lunaria biennis*. EUGÈNE HAIRS (*Bull. Acad. roy. Belg.*, 1909, 1042—1048).—The seeds yield about 1% by weight of an alkaloidal residue containing a well-defined, crystalline alkaloid and possibly a second similar substance.

The crystalline alkaloid, m. p. 220° (decomp.), isolated and purified in the usual way, forms slender, colourless needles, possesses a bitter taste, and dissolves readily in chloroform, but is scarcely soluble in ether or water. It is distinctly alkaline in reaction, dissolves readily in dilute acids, and gives precipitates with the usual alkaloidal reagents. Unlike the alkaloids, sinapine and cheiroline, already isolated from plants of the same natural order (*Cruciferae*), it does not contain sulphur.

T. A. H.

Formation of Glucosides by means of Plants. GIACOMO L. CIMICIAN and CIRO RAVENNA (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 594—596. Compare Abstr., 1909, ii, 604).—Not only living maize

plants, but also the pasty mass obtained by triturating them with water, are able, in presence of toluene, to decompose salicin and to transform saliginin, catechol, and, possibly, quinol and mandelonitrile into glucosides which are decomposed by emulsin.

T. H. P.

Occurrence of Formic Acid in Raspberries. A. RÖHRIG (*Zeitsch. Nahr. Genussm.*, 1910, 19, 1—8).—The author has investigated the question of the occurrence of formic acid in fruits, more particularly in raspberries, the matter being of some importance seeing that this acid is employed to preserve fruits and fruit-juices and that the quantity thus added has to be estimated. He finds that fresh raspberries contain 0.000176% of formic acid, a quantity that would scarcely come into consideration when dealing with the amounts of formic acid used for preservative purposes. The method described by Wegner (*Abstr.*, 1903, ii, 700) was employed for estimating the formic acid, it having been found to be the most trustworthy. As regards the fact that lactic acid also yields carbon monoxide when heated with sulphuric acid, the author shows that the volatile acids obtained from raspberries contain only a trace, if any, of this acid.

W. P. S.

Influence of Cultivation on the Alkaloid-content of Certain Solanaciæ. J. CHEVALIER (*Compt. rend.*, 1910, 150, 344—346).—The yield of alkaloids obtained from specially cultivated plants can be considerably increased by the employment of an appropriate manure. In experiments carried out on a large scale, it was found that *Belladonna* plants yielding 0.32—0.33% of alkaloids under ordinary conditions of cultivation, gave 0.48—0.49% when manured with phosphates and 0.40—0.61% when treated with nitrates. Under certain conditions a nitrogenous manure gave 0.73% of alkaloids for the dried leaves. Similar results were obtained in experiments on *Datura stramonium* and *Hyoscyamus*.

W. O. W.

Occurrence of Anisyl Alcohol and Anisaldehyde in the Fruit of Tahiti Vanilla. HEINRICH WALBAUM (*Festschrift Otto Wallach*, 1909, 649—653).—Vanilla from Tahiti has not the same aroma, and is not so valuable as that from Mexico or Réunion; it is found to contain anisic acid, anisaldehyde, anisyl alcohol (*p*-methoxybenzyl alcohol), and very small quantities of substances which have not been isolated and have an intense odour. The occurrence of *p*-methoxybenzyl alcohol in nature has not been observed previously.

W. H. G.

Behaviour of Plants towards Lithium Salts. CIRO RAVENNA and M. ZAMORANI (*Atti R. Acad. Lincei*, 1909, [v], 18, ii, 626—630).—It is usually supposed that lithium has a highly toxic action on higher plants. Finding that the ash of tobacco leaves contains sufficient lithium to impart a marked coloration to a flame, the authors have investigated the effect of lithium sulphate on various plants. On tobacco and the potato, this salt has no toxic action, but with oats and, to a still greater extent, with beans, there is a distinct poisoning effect.

T. H. P.

Accumulation of Nitrogen in Soils. A. KRAINSKY (*Centr. Bakt. Par.*, 1910, ii, 26, 231—235).—Liquid cultures of *Azotobacter* utilise 100—200 units of sugar for 1 of nitrogen fixed. In sand cultures, owing to better aeration, the amount of carbon used is 11—30 units to 1 of nitrogen fixed. The economy of organic matter in soils is attributed to the co-operation of autotrophic organisms which in absence of light produce organic compounds by the decomposition of carbon dioxide with liberation of oxygen.

N. H. J. M.

Use of Boron as a Catalytic Manure. H. AGULHON (*Compt. rend.*, 1910, 150, 288—291. Compare this vol., ii, 241).—The addition of boric acid to a nutrient sterile medium in which wheat was grown has been found to be distinctly beneficial to the plants, unless added in amounts greater than 0.01 gram per 1000 grams of medium, when germination is prevented and the plants become etiolated. Similar results were obtained in experiments carried out under natural conditions in earth. The increased yield (calculated on the dried plant) amounted to 50% with maize, 21% with rape-seed, and 32% in the case of turnips, when a dose of 0.5 gram of boric acid per sq. metre was employed. No distinct increase occurred in the case of peas or oats. Estimation of boron in the ash showed that plants grown under these conditions contained only the normal proportion of this element.

W. O. W.

Manuring with Carbon Dioxide. EILHARD A. MITSCHERLICH (*Landw. Jahrb.*, 1910, 39, 157—166).—Two series of pot experiments are described, in which oats were grown in three different soils (sandy soil, loam, and peat soil) without manure, with complete manure, and with manures in which phosphoric acid, nitrogen, and potassium respectively were wanting. The one series was watered with tap-water, the other with water saturated with carbon dioxide.

The results showed that no increased yield was obtained by increasing the amount of carbon dioxide in the soil. A small amount of carbon dioxide rapidly increases the solubility of sparingly-soluble plant nutrients, and it would seem that under natural conditions the soil almost always contains sufficient carbon dioxide, either given off by roots or produced by the oxidation of organic matter. Application of substances for the production of carbon dioxide in the soil is therefore unnecessary.

N. H. J. M.

Actions of Zinc in Pot Experiments. Contribution to the Ammonia Question. II. PAUL EHRENBURG (*Landw. Versuchs-St.,* 1910, 72, 15—142. Compare Abstr., 1908, ii, 1068).—It is shown that the employment of zinc may obscure the results of pot experiments by acting sometimes favourably and sometimes unfavourably. Soils having unfavourable physical properties may be improved by the presence of zinc, especially when manured with sodium nitrate. As regards the effect of zinc on manures, it is shown that when ammonium salts are employed, the zinc may liberate a portion of the ammonia, which will act injuriously on the roots of the plants. Under sterilised

conditions, the injury will be much greater, owing to the absence of nitrification. Other possible modes of action are discussed, such as the stimulating action of zinc on plants, the poisonous effects of zinc dissolved by acid soils, etc., and the conclusion is drawn that the use of zinc should be avoided in vegetation experiments, in drainage experiments, and for collecting rain-water when the amounts and condition of the nitrogen are to be determined.

N. H. J. M.

Analytical Chemistry.

Micro-chemistry with Special Reference to Behrens' Work. FRIEDRICH EMICH (*Ber.*, 1910, 43, 10—45).—A general review of the methods adopted in studying the properties of chemical substances and in their detection and estimation.

J. J. S.

Automatic Gas Analysis Apparatus. KARL HOHMANN (*Festschrift Otto Wallach*, 1909, 478—495).—A somewhat complicated apparatus is described, in which one or more gas measuring tubes are combined with the ordinary Orsat pipettes, and in which the various operations involved in the exposure of the gas mixture to the absorbing reagents are effected automatically. The apparatus is designed in such a way that it can be used either with water or with mercury,

H. M. D.

Gas-volumetric Estimation of Hydrogen by Catalytic Absorption. CARL PAAL and WILHELM HARTMANN (*Ber.*, 1910, 43, 243—258).—Colloidal palladium, prepared by the method of Paal-Amberger (*Abstr.*, 1904, ii, 180; 1905, ii, 397), will absorb 300—400 times its volume of hydrogen. If the palladium-sol also contains a reducible substance, the latter is reduced by the hydrogen, and the palladium may be used to absorb further quantities of hydrogen. The authors show that this reaction may be used for the estimation of hydrogen in gaseous mixtures. The reducible substance used is sodium picrate, 2 : 4 : 6-triaminophenol being formed. The palladium-sol is contained in a modified form of Hempel pipette, and the hydrogen absorbed in the usual way. The time of absorption varies from ten to one hundred and twenty minutes, according to the mixture to be analysed. The method was tested on mixtures of hydrogen with: (1) oxygen, (2) nitrogen, (3) air, (4) carbon monoxide, (5) carbon monoxide and nitrogen, (6) carbon monoxide and air, (7) unsaturated gaseous hydrocarbons, (8) ethane, (9) ethane and nitrogen, (10) ethane and air, (11) ethane and carbon monoxide. It was also tested on coal gas. In each case the absorbable constituents other than hydrogen were absorbed by the usual reagents before absorbing the hydrogen.

It was found that when oxy-hydrogen gas was treated with the palladium-picrate-sol, it was catalysed to water, the picrate not being reduced.

T. S. P.

New Reagent for Hydrogen Peroxide. K. W. CHARITSUKOFF (*Chem. Zeit.*, 1910, 34, 50).—A strip of filter-paper is drenched in a solution of cobalt naphthenate in benzene and then dried. The rose-coloured paper turns at once an olive-green when moistened with even very weak solutions of hydrogen peroxide.

By suddenly directing a flame on a piece of ice, traces of hydrogen peroxide will be formed, and may be detected in the liquid.

L. DE K.

The Effect of Continued Grinding on Water of Crystallisation. IRVING B. BLEEKER (*Chem. News*, 1910, 101, 30).—On continued grinding for two hours in an ordinary Wedgwood mortar, magnesium sulphate lost 2.55%, disodium hydrogen phosphate 1.85%, and aluminium potassium sulphate 0.49%, of water of crystallisation. In the case of barium chloride, however, the salt became moist and sticky, and the amount of water was increased by 2.11%. Magnesium sulphate also became moist at first, but soon changed again to a dry and powdery condition.

L. DE K.

Estimation of Chlorates in the Presence of Nitrates and Chlorides. TARAK NATH DAS (*Chem. News*, 1910, 101, 38—39).—The solution is heated in a specially constructed flask with excess of sodium hydroxide and a definite amount of standardised stannous chloride in a current of hydrogen. The exit tube dips into a beaker containing standard iodine solution made alkaline with sodium hydrogen carbonate. When the liquid boils and the reduction is complete, the flask is cooled suddenly, thus causing the iodine to enter the flask. The solutions of the flask and beaker, together with the washings of the whole apparatus, are collected, and the excess of iodine is estimated as usual.

The iodine used in the reaction represents the excess of stannous chloride, and the stannous chloride oxidised represents the chlorate.

L. DE K.

Apparatus for the Estimation of Sulphur in Iron and Steel. GEORG PREUSS (*Zeitsch. angew. Chem.*, 1910, 23, 250).—An improvement on the apparatus described previously (*Abstr.* 1909, ii, 933). The Kipp apparatus is dispensed with, and no water need circulate through the cooler. The recoil valve introduced in the little tube inside the absorption vessel prevents all regurgitation of the liquid, and the apparatus, therefore, does not want constant attention even when there is no carbon dioxide pressure.

The flask is filled with the required amount of hydrochloric acid. D 1.52, and the absorption vessel filled with cadmium solution. The weighed sample of iron or steel is now dropped into the acid, and the cooling arrangement is then instantly put on and sealed with water. The ground joint of the cooler has at the top and the bottom a small circular opening; in the ground joint of the neck of the flask there is a small rabbit. By means of a washbottle, a cold 5% solution of sodium hydrogen carbonate is introduced through the upper hole of the cooler, and the flask is then at once heated with a small flame

until the material has completely dissolved. By turning the stopper on to the rabbit in the neck of the flask, the soda solution runs into the flask, and the carbon dioxide evolved forces any remaining hydrogen sulphide into the cadmium solution. If it should be necessary to use hydrochloric acid, D 1.19, a special washing arrangement (see the author's previous paper) must be used. L. DE K.

Estimation of Total Sulphur in Urine. STANLEY R. BENEDICT (*J. Biol. Chem.*, 1910, 7, 101—102).—A criticism of Ritson's paper (*Abstr.*, 1909, ii, 827).

Desulphitation of Wine by means of Hexamethylenetetramine. ROUILLARD and GOUJON (*Ann. Patisf.*, 1910, 3, 14—16).—Attention is drawn to the fact that hexamethylenetetramine is being used to remove excess of sulphurous acid from wines; in an acid solution, such as wine, hexamethylenetetramine undergoes decomposition with the production of formaldehyde, which combines with the sulphurous acid. The portion of the latter acid thus combined is not readily liberated on boiling the wine with the addition of phosphoric acid, and, consequently, the ordinary methods of estimating sulphurous acid in wine yield too low results should the wine have been treated with hexamethylenetetramine. The aldehyde-sulphurous acid compound formed is, however, not absolutely stable, and by acidifying such a wine with sulphuric acid and distilling, it is possible to detect formaldehyde in the distillate by means of the usual magenta-sulphurous acid reagent. White wines may be tested directly with this reagent, and the test may also be applied to red wines, without distillation, if the colouring matters is first removed by treatment with animal charcoal; in either case the wine must be acidified with sulphuric acid before the test is applied. Experiments made by the authors show that treatment with hexamethylenetetramine will apparently "remove" 75% of the sulphurous acid from a wine containing 100 milligrams of sulphurous acid per litre. W. P. S.

Volumetric Estimation of Sulphuric Acid by the Barium Chromate Method. M. HOLLIGER (*Zeitsch. anal. Chem.*, 1910, 49, 81—93).—A slight modification of Andrews' method. The neutralised sulphate solution is heated to boiling, and precipitated by adding barium chromate emulsion, cleared just before use, with a sufficiency of hydrochloric acid. After adding a few drops of ferric chloride, the undecomposed barium chromate is precipitated by ammonia in slight excess. The filtrate and washings are then mixed with 20 c.c. of hydrochloric acid, and diluted to 400 c.c. The soluble chromate formed by the action of the sulphate on the barium chromate, which, therefore, represents the sulphuric acid, is then estimated iodometrically as usual. L. DE K.

The Heat of Chemical Reactions as a Basis for a New Analytical Method. HENRY HOWARD (*J. Soc. Chem. Ind.*, 1910, 29, 3—4).—*Assay of fuming sulphuric acid.*—One hundred grams of the sample are weighed in a Dewar vacuum tube, 100 x 45 mm., and the

temperature (*a*) is noted. One hundred grams of exactly 92% sulphuric acid (temp. *b*) are added with stirring, and the end temperature (*c*) is noted. The heat of the reaction is represented by $c - (a + b)/2$, and reference is then made to a table showing the percentage of free sulphur trioxide (from 21—26%).

Assay of ordinary (96%—99%) sulphuric acid.—One hundred grams are weighed in the Dewar tube, and the temperature (*a*) is noted. One hundred grams of fuming acid (24—25% of free sulphur trioxide) (temp. *b*) are added, and the end temperature (*c*) is noted. The heat of the reaction is represented by $c - (a + b)/2$, and reference is then made to a table showing the percentage of hydrogen sulphate (from 96.6—99%).

The principle of the method may, of course, be applied in a large number of other cases, for instance, an alkali might be estimated by noting the rise in temperature on adding acid, etc. L. DE K.

Gas-volumetric Analysis with the "Decomposition Flask," and the Estimation of Nitrogen in Smokeless Powders. ERNST BERL and A. W. JURRISEN (*Zeitsch. angew. Chem.*, 1910, 23, 241—248).—The apparatus consists essentially of a strong, round-bottomed flask of 250—300 c.c. capacity. By means of a ground joint, a glass hood is attached, which carries at one side a dropping funnel, with a glass stopcock, and at the other side a capillary tube closed with a three-way stopcock. By turning the latter in the proper positions, communication may be established with a water air pump, or with the Lunge nitrometer.

The analysis is carried out by treating the substance with sulphuric acid and a little mercury in a vacuum; sometimes a preliminary oxidation with chromic acid is required. The impure nitric oxide liberated, which must undergo further tests, is expelled from the flask by means of a saturated solution of sodium sulphate, and transferred to the Lunge burette. L. DE K.

Distilling Apparatus for Nitrogen Estimations by Kjeldahl's Method. WOLFGANG HEBNER and GEORG WIEGNER (*J. Landw.*, 1910, 57, 385—390).—A new form of bulb for attaching to the distilling flask is described with sketch. The bulb is stated to be very efficacious in preventing alkali from being carried over without prolonging the distillation. When zinc is employed, a similar bulb partly filled with glass beads is recommended. N. H. J. M.

[Modification of] Ronchèse's Method of Estimating Ammonia. JOHN M. WILKIE (*J. Soc. Chem. Ind.*, 1910, 29, 6—7).—The author has slightly modified Ronchèse's formaldehyde method so as to render it more generally applicable.

A *N*/10 solution is made of ammonium sulphate; a *N*/5 one in the case of other mineral ammonium salts; 10 c.c. of the liquid are then made exactly neutral to methyl-orange (methyl-red is still better), and 20 c.c. of 10% formaldehyde, neutralised immediately before use, are added. The liberated acid, which represents the ammonia, is then titrated with *N*/20-barium hydroxide, using phenolphthalein as

indicator. If the water used is quite free from carbon dioxide, the end reaction will be very sharp.

Organic salts of ammonia, provided their reaction is neutral, may also be estimated by this process. Hexamethylenetetramine may be converted into ammonium sulphate by heating with sulphuric acid, and then be treated as directed.

L. DE K.

Iodometric Estimation of Phosphoric Acid. PAUL ARTMANN [and R. BRANDIS] (*Zeitsch. anal. Chem.*, 1910, 49, 1—25).—The process is based on the determination of the ammonia contained in ammonium phosphomolybdate. One gram of the phosphate is dissolved in nitric acid with addition of a little hydrochloric acid; the solution is freed from sulphates by means of barium nitrate, and finally made up to 250 c.c.; 25 c.c. are then taken for analysis. The yellow precipitate obtained in the ordinary way is washed, by decantation, with water, and then dissolved in 4—5 c.c. of 2*N*-sodium hydroxide; the filter is moistened with a little *N*/2-alkali, and then washed with 40—50 c.c. of water. To the solution are then added 20 c.c. of hypobromite solution (7.5 grams of bromine per litre), the strength of which has been carefully ascertained by titration. The liquid is now saturated with sodium hydrogen phosphate (8—10 grams), and 1.5 grams of potassium iodide are added; 15 c.c. of 4*N*-sulphuric acid are now added, and the iodine liberated is then titrated as usual with *N*/10-thiosulphate.

The percentage of phosphoric acid (*c*) is calculated from the formula $x = a(b - c)/0.016088d$, in which *a* = grams of iodine per 1 c.c. of thiosulphate, *b* = c.c. of thiosulphate used for 20 c.c. of hypobromite, *c* = c.c. of thiosulphate used in the final titration, and *d* = quantity (1 gram) weighed out for analysis.

Further experiments as to the suitability of the process for technical purposes are in progress.

L. DE K.

Estimation of Arsenic in Copper. E. AZZARELLO (*Gazzetta*, 1909, 39, ii, 450—453).—The author has modified the apparatus and method devised by Holland and Bertaux (*Abstr.*, 1900, ii, 438) for estimating small quantities of arsenic so as to render the estimation more rapid and trustworthy.

T. II. P.

Detection of Minute Quantities of Boron in the Organism and in Complex Mixtures. GABRIEL BERTRAND and H. AGULHON (*Ann. Chim. anal.*, 1910, 15, 45—53 *).—The ash obtained is distilled with a little sulphuric acid and methyl alcohol, and the distillate is received in a platinum crucible containing a few drops of *N*-sodium hydroxide. The distillation is repeated after adding a little more methyl alcohol, and the mixed distillate is then evaporated to dryness.

The Turmeric Test.—The residue is dissolved in 1 c.c. of water, and acidified with hydrochloric acid. A strip of delicate turmeric paper is introduced in such a manner that only a small part of it dips into the liquid, and the other part is bent over the side of the crucible, which is then covered with a watch-glass. After a few minutes, or a few hours, according to the amount of boric acid present, the extreme

and *Bull. Soc. chim.*, 1910, [iv], 7, 90—99.

end of the paper turns orange-red, and then bluish-violet on moistening with ammonia; this way is preferable to the drying at a higher temperature.

The Flame Test.—The alkaline residue is mixed with a pinch of finely-powdered calcium fluoride and a drop of sulphuric acid. A platinum wire is dipped in, and introduced in the extreme end of a pure hydrogen flame; the boron fluoride will then cause a green coloration, which may be examined spectroscopically. L. DE K.

Use of Lead Peroxide in Organic Combustions. HUGO WEILL (*Ber.*, 1910, 43, 149).—Commercial lead peroxide always evolves carbon dioxide when heated. Samples after warming with nitric acid, or heating at 150° with syrupy phosphoric acid, still invariably give carbon dioxide when heated at 280° in a combustion tube. Material freed in this manner may be used for six or eight combustions with satisfactory results; it then absorbs carbon dioxide, and low results are obtained in the analysis. When more strongly heated, the carbon dioxide is again eliminated. The use of lead peroxide is therefore to be avoided. E. F. A.

Estimation of Carbon, Hydrogen, and Nitrogen in Highly Combustible Liquids. ERNST BERL (*Zeitsch. angew. Chem.*, 1910, 23, 249).—Instead of weighing the liquid intended for organic combustion in small glass bulbs, the requisite quantity is dropped from a weighing pipette on to copper oxide contained in little goblets made from fine copper wire gauze. Before use these are first heated in a copper crucible and cooled in a desiccator. L. DE K.

A Simple Burette for the Estimation of Carbon Dioxide. H. H. STEPHENSON (*Chem. News*, 1910, 101, 61).—The burette resembles a Bunte burette fitted with a three-way stopcock at each end. One tube from the lower stopcock (*B*) is connected by a rubber tube to a bottle (*C*) containing water, and the other tube to a bottle (*D*) containing aqueous sodium hydroxide, D 1.28. When required for use, (*C*) is first raised until the burette is filled. The gas, after running for a moment through the exit way of the upper stopcock (*A*), is connected with the burette, and 100 c.c. of the gas measured in the usual way. (*A*) being closed, (*C*) is lowered until the water just appears in the burette above the stopcock (*B*). The cock is turned to connect with (*D*), and the absorption of the carbon dioxide accelerated by shaking the burette and lowering the bottle (*D*). The volume of the gas is then again read off with the usual precautions. L. DE K.

Assay of Calcium Carbide, Sodium Amalgam, and Zinc Dust with the "Decomposition Flask." ERNST BERL and A. W. JURRISEN (*Zeitsch. angew. Chem.*, 1910, 23, 248–249).—These substances may be conveniently tested by means of the authors' decomposition flask (this vol., ii, 240). Calcium carbide is decomposed in the evacuated flask with water saturated with acetylene, and by filling the glass with the same liquid, all the gas evolved is transferred to the measuring burette, the water-seal of which is also saturated with acetylene.

Sodium amalgam is decomposed with acidified water, and the hydrogen expelled from the flask by means of brine. Before measuring, any carbon dioxide is absorbed with potassium hydroxide.

Zinc or zinc dust is dissolved in hydrochloric acid with a drop of platinum chloride to accelerate the action, but copper sulphate should not be used for that purpose. Before dissolving the zinc, the air from the flask must be swept out completely by a current of carbon dioxide.

L. DE K.

Quantitative Separation of Calcium and Magnesium in the Presence of Phosphates and Small Amounts of Iron, Devised especially for the Analysis of Foods, Urine, and Faeces. FRANCIS H. MCCRUDDEN (*J. Biol. Chem.*, 1910, 7, 83—100, 201).—Two drops of alizarin solution are added to the solution, then ammonia until just alkaline, and then hydrochloric acid until just acid; 10 c.c. of $N/2$ -hydrochloric acid and 10 c.c. of 2.5% oxalic acid are then added, and the mixture is boiled; a small amount of ammonium oxalate is added gradually to the boiling solution, which is then allowed to cool; when cold, 8 c.c. of 20% sodium acetate solution are added slowly and with constant stirring. It is then left for four to eighteen hours, filtered, and the precipitate is washed free from chlorides with 1% ammonium oxalate solution. The precipitate is then incinerated with the filter paper and weighed. The filtrate, which contains the magnesium, is evaporated nearly to dryness with nitric acid; 10 c.c. of hydrochloric acid are added, and again evaporated nearly to dryness, diluted, nearly neutralised with ammonia, and cooled; then disodium hydrogen phosphate and ammonia are added, and the magnesium weighed as pyrophosphate in the usual way with certain precautions, which are described in full. If iron is present, sodium citrate solution is added before the magnesium is precipitated.

W. D. H.

Influence of Manganese on the Estimation of Magnesium in Soils. P. DE SORNAY (*Bull. Assoc. Chim. Sucr. Dist.*, 1910, 27, 671—675).—Precipitation with ammonium hydroxide fails to remove the whole of the manganese present, and on adding sodium phosphate, a precipitate, consisting of ammonium magnesium phosphate and ammonium manganous phosphate, with a trace of manganous hydroxide, is obtained. Attempts to eliminate the whole of the manganese before precipitating the magnesium were unsuccessful, owing, it is supposed, to the presence of ammonium salts. Bromine water failed to oxidise the manganese completely; and when ammonium sulphide is employed, most of the magnesium remains in the precipitate.

The method adopted was to ignite the sodium phosphate precipitate and determine the manganese present by Leclerc's method. In one soil it was found that the precipitated phosphates contained more than 50% of manganese.

N. H. J. M.

New Volumetric Methods for Titrating Zinc or Lead. ERWIN RUPP (*Chem. Zeit.*, 1910, 34, 121).—*Zinc*.—10—20 c.c. of an approximately $N/2$ -solution of pure potassium cyanide, which has been checked

ABSTRACTS OF CHEMICAL PAPERS.

with $N/2$ -hydrochloric acid, are placed in an Erlenmeyer flask; little water and 0.3—0.5 gram of ammonium chloride are added, and the neutralised zinc solution is then added, while rotating the bottle until a permanent cloud is produced. One c.c. of $N/2$ -cyanide = 0.008171 gram of zinc. If pure cyanide is not available, the cyanide may be checked with a standard zinc sulphate solution neutral to methyl-orange in presence of ammonium chloride.

Lead.—To 20—25 c.c. of pure $N/2$ -cyanide, checked with $N/2$ -hydrochloric acid and methyl-orange, is added a definite volume of lead nitrate solution neutral to methyl-orange; the whole is made up to 100 c.c., and in 50—70 c.c. of the filtrate the excess of cyanide is estimated with $N/2$ -hydrochloric acid. The difference between the titrations represents the lead; 1 c.c. of $N/2$ -acid = 0.05178 gram of lead.
L. DE K.

Estimation of Cinnabar and Sulphur Auratum in Rubber Wares. FRITZ FRANK and KARL BIRKNER (*Chem. Zeit.*, 1910, 34, 49—50. Compare Abstr., 1909, ii, 833).—0.5 Gram of the cut-up sample is placed in a 100 c.c. round-bottomed flask, and 10 grams of ammonium persulphate and 10 c.c. of fuming nitric acid (D 1.5) are added. The action starts in the cold, and when, after a few minutes, it is practically over, it must be completed by heating moderately on a sand-bath for fifteen to twenty minutes. Should the oxidation be still incomplete, another 3 grams of persulphate should be added little by little. The mass, which on cooling forms a solid cake, is then dissolved in hot water, if necessary, after addition of about 10 c.c. of hydrochloric acid.

The solution, which contains all the antimony and mercury present, and also the joint sulphur as sulphuric acid, is then analysed for these substances as usual. If no great accuracy is required, it is sufficient to weigh jointly the sulphides of mercury and antimony freed from excess of sulphur; extraction with yellow ammonium sulphide will leave the mercury sulphide undissolved.
L. DE K.

Reaction of Titanium. HENRY J. H. FENTON (*Ber.*, 1910, 43 267—268).—Piccard (*this vol.*, i, 67) has suggested that the colour obtained with dihydroxymaleic acid and compounds of quadrivalent titanium is due to tervalent titanium formed by the reducing action of the dihydroxymaleic acid. The author had previously suggested the reaction as a very delicate test for quadrivalent titanium (*Trans.*, 1908, 93, 1961). Further experiments have shown that tervalent titanium gives a different coloration from quadrivalent titanium. In moderately dilute solutions the latter gives a brilliant orange colour, whereas the former gives a dull yellowish-brown, which is only changed to orange on oxidation by atmospheric oxygen.
T. S. P.

Microchemical Detection of Tannins. LUIGI E. CAZZA (*Zeitsch. wiss. Mikroskopie*, 1909, 26, 59—64).—See *this vol.*, ii, 233.

